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## (54) ACRYLAMIDE POLYMER AND ITS USE

(57)Abstract:

PURPOSE: To obtain a paper reinforcement which is an aqueous solution of a high-mol. acrylamide polymer, has a low viscosity in spite of the high concentration, and is excellent in paper strengths, e.g. burst index and Z-axis strength, and in freeness.

CONSTITUTION: This acrylamide polymer has a weight-average mol.wt. (a) of 1,500,000-10,000,000, a weight-average inertia radius (b) of 30-150nm, and a (b) to (a) ratio, as an index to the average degree of crosslinking, of 0.00004 or lower; and an aqueous solution of the polymer has a weight-average mol.wt. of 500,000-10,000,000, a polymer concentration of 22-60% and a viscosity as measured at 25° C with a Brookfield viscometer of 50,000cPs or lower.

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## CLAIMS

[Claim(s)]

[Claim 1] The acrylamide system polymer whose weight average molecular weight (a) is 1,500,000-10,000,000, whose weighted mean radius of inertia (b) is 30-150nm and whose ratio [ of a weighted mean radius of inertia (b) and weight average molecular weight (a) ] (b)/(a) is 0.00004 or less.

[Claim 2] The acrylamide system polymer according to claim 1 whose number average molecular weight (c) is 400,000-5,000,000 and whose weight-average-molecular-weight (a) and ratio [ of (c) ] (a)/(c) is six or less.

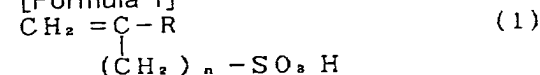
[Claim 3] The acrylamide system polymer according to claim 2 characterized by including a with a molecular weight of 1,000,000 or more polymer 40% of the weight or more.

[Claim 4] The acrylamide system polymer according to claim 1 whose Brookfield viscosity [ in / in the Brookfield viscosity in 25 degrees C of a 10 % of the weight water solution / 25 degrees C of 20 to 10,000 centipoise or a 15 % of the weight water solution ] is 100 to 30,000 centipoise.

[Claim 5] The acrylamide system polymer according to claim 4 whose diameter of hydration by dynamic light scattering is 50-300nm.

[Claim 6] a general formula -- one sort or the acrylamide system polymer according to claim 1 which uses two or more sorts, and is reacted and obtained of the compounds shown by (1 [-izing 1]), and/or those salts.

[Formula 1]



(For the inside R of a formula, a hydrogen atom or a low-grade alkyl group, and n are the integer of 1-8)

[Claim 7] The acrylamide system polymer according to claim 6 which contains the compounds shown by the general formula (1), and/or those salts as one sort or a two or more sort copolymerization component.

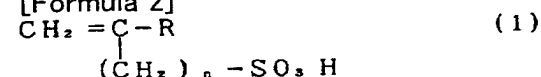
[Claim 8] The acrylamide system polymer according to claim 6 characterized by containing a cross-linking monomer as a copolymerization component.

[Claim 9] The paper reinforcing agent which comes to contain the acrylamide system polymer of a publication in any 1 term of claims 1-8.

[Claim 10] The acrylamide system polymer water solution whose polymer concentration is the range which is 22 - 60%, whose Brookfield viscosity in 25 degrees C is below 50,000cps (centipoise) and whose weight average molecular weight is 500,000-10 million.

[Claim 11] the following general formula -- the acrylamide system polymer water solution according to claim 10 obtained by carrying out a polymerization using one sort or two sorts or more of vinyl compounds chosen from the vinyl compounds expressed with (1 [-izing 2]), and/or those salts.

[Formula 2]



(For the inside R of a formula, a hydrogen atom or a low-grade alkyl group, and n are the integer of 1-8)

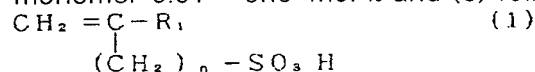
[Claim 12] The acrylamide system polymer water solution according to claim 11 which contains one sort or two sorts or more of vinyl compounds chosen from the vinyl compounds expressed with a general formula (1), and/or those salts as a copolymerization component.

[Claim 13] The acrylamide system polymer water solution according to claim 11 characterized by containing a cross-linking monomer as a copolymerization component.

[Claim 14] The acrylamide system polymer water solution according to claim 13 characterized by being obtained by the half-batch polymerization which trickles a monomer continuously.

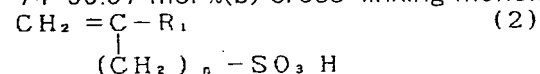
[Claim 15] The paper reinforcing agent which comes to contain the acrylamide system polymer of a publication in any 1 term of claims 10-14.

[Claim 16] (a) (meta) [Formula 3] expressed with the acrylamide 94-99.98 mol % (b) cross-linking monomer 0.01 - one-mol % and (c) following general formula (1)



(The inside R<sub>1</sub> of a formula is a hydrogen atom or the low-grade alkyl group of carbon numbers 1-3, and n is the integer of 1-4) The paper reinforcing agent characterized by consisting of a water-soluble polymer obtained [ make / into a constituent / 0.01-5 mol % of one sort or 2 sorts or more of vinyl compounds chosen from vinyl compounds and/or those salts ] by carrying out a polymerization.

[Claim 17] (a) (meta) [Formula 4] expressed with the (c) following general formula (2) acrylamide 74-99.97 mol % (b) cross-linking monomer 0.01 - one-mol %



0.01-5 mol % of one sort or 2 sorts or more of vinyl compounds chosen from vinyl compounds and/or those salts, (The inside R<sub>1</sub> of a formula is a hydrogen atom or the low-grade alkyl group of carbon numbers 1-3, and n is the integer of 1-4) And the paper reinforcing agent characterized by consisting of a water-soluble polymer obtained by carrying out the polymerization of the vinyl compound [ which were chosen from the vinyl compounds in which the (d) above-mentioned monomer and copolymerization are possible, and/or those salts / one sort or two sorts or more of ] 0.01 - 20-mol %.

[Claim 18] Paper using a paper reinforcing agent according to claim 9, 15, 16, or 17.

[Translation done.]

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to a useful acrylamide system polymer and its water solution in paper manufacture industry, the waste-water-treatment field, the engineering-works construction field, etc. Specifically, it is related with the acrylamide system polymer which controlled the branching structure of cross linkage. The acrylamide system polymer of this invention is useful especially as a paper reinforcing agent excellent in the paper durability enhancing effect in a paper manufacture industrial field.

[0002]

[Description of the Prior Art] The acrylamide system polymer is used for various applications from before. Specifically, a paper reinforcing agent, a filtration improvement agent, the yield improver, the flocculant, the object for the secondary productions of petroleum, the dispersant, etc. are known. For those applications, the acrylamide system polymer from about 100,000 to 20 million or more things with various weight average molecular weight is properly used by the purpose, and the polymer which has the straight chain-like molecular structure has mainly been used.

[0003] Molecular weight is made to increase, a paper reinforcing agent etc. giving the partial structure of cross linkage and branching structure, and controlling a viscosity rise of those solutions by using a cross linking agent for an acrylamide system polymer etc., in a paper manufacture industrial field, in recent years, and the attempt which aims at improvement in the engine performance is made.

[0004] For example, the technique which uses the vinyl monomer which has two or more double bonds is in a molecule as a cross linking agent. As a concrete vinyl monomer, 3 functionality monomers, such as divinyl monomers, such as methylenebis acrylamide, methylenebis meta-acrylamide, ethylene glycol diacrylate, and ethylene glycol dimethacrylate, 1 and 3, 5-thoria chestnut roil hexahydro-S-triazine, and triallyl isocyanurate, etc. are known. About the macromolecule quantification technique by the crosslinking reaction only depending on these vinyl monomer, the heterogeneity of the branching structure of cross linkage is large, and the phenomenon of the gelation effectiveness amplifying about polyfunctional monomer is seen, and it can be said that it is still inadequate as a paper reinforcing agent.

[0005] Furthermore, in addition to these cross linking agents, the attempt which manufactures the acrylamide system polymer which has the branching structure of cross linkage is also made by using a specific compound together. For example, combination with the monomer which has a cross linking agent, the 1st class amine, or a hydroxyl group or combination, a cross linking agent and a specific hydrophobic monomer, and the combination which it is with a cross linking agent and an itaconic-acid derivative further are known. However, although macromolecule quantification is attained by hypoviscosity, the result is also fully as a paper reinforcing agent insufficient [ seen from the structure side of a polymer ] also in any, still.

[0006] Moreover, the attempt which manufactures the acrylamide system polymer which has the branching structure of cross linkage also with means other than the branching bridge formation approach by copolymerization using the aforementioned polyfunctional vinyl system monomer is

made. The additive for paper manufacture using a reaction with a specific N-permutation acrylamide derivative like N,N-dimethylacrylamide as the example, a persulfuric acid system, or a peroxide system catalyst is proposed. However, although macromolecule quantification is enabled by hypoviscosity about this approach, since the cutting reaction of a polymer chain is also produced, the obtained polymer cannot fully say the effectiveness as a paper reinforcing agent as sufficient thing seen from that structure side, either.

[0007] Moreover, the acrylamide system polymer manufactured in these conventional techniques is usually used for the above-mentioned application as a water solution, it is possible to make it the water solution of concentration 15%, and the manufacture approach of a thing that molecular weight is about 3 million is proposed. However, \*\* et al. and a high-concentration thing are not known at all, but the concentration is at most 15% - 21%. The reason is that macromolecule quantification which is expected is not made or viscosity becomes very high by the straight chain-like polymer by the concentration beyond this. Moreover, it is because it will become unusable as a paper reinforcing agent -- crosslinking reaction advances unusually, the whole gels and it being high concentration and an interval are not partially obtained in the state of a water solution, or insoluble gel is formed in water -- if it is going to introduce the branching structure of cross linkage into a polymer.

[0008] Although the surface paper durability agent which becomes JP,3-279491,A from the polyacrylamide system polymer water solution of 500 to 5000 cps viscosity and 10 - 30% of concentration is indicated and the range of molecular weight 100,000-3 million is indicated in it, in this approach, there is no concrete description which can attain with a molecular weight of 500,000 or more macromolecule quantification absolutely above 22% concentration.

[0009] Although the improvement in polymer concentration had a merit in respect of the transportation cost, the amount acrylamide system polymer water solution of macromolecules of 22% or more of concentration was not known at all for the above reasons until now.

[0010]

[Problem(s) to be Solved by the Invention] The purpose of this invention offers the acrylamide system polymer water solution which has the new physical properties which are not known, the acrylamide system polymer water solution which is hypoviscosity comparatively in high concentration in spite of being specifically the amount of macromolecules, and its manufacture approach with the conventional technique.

[0011] Other purposes of this invention are offering the acrylamide system polymer which has the new structure which is not known for the above conventional techniques.

[0012] Furthermore, other purposes of this invention are offering the paper reinforcing agent which consists of this acrylamide system polymer.

[0013]

[Means for Solving the Problem] As a result of repeating examination wholeheartedly about the polymerization of an acrylamide system polymer in view of the above-mentioned situation, this invention persons came to acquire the aqueous polymerization object which is hypoviscosity, though it was the high concentration which is not seen by the former and the amount of macromolecules.

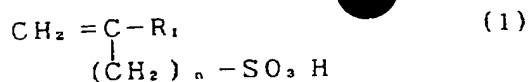
[0014] That is, weight average molecular weight (a) is 1,500,000-10,000,000, it is 150nm and the weighted mean radius of inertia (b) of this invention is the acrylamide system polymer the weighted mean radius of inertia (b) as an index which shows an average degree of cross linking, and whose 30 - ratio [ of weight average molecular weight (a) ] (b)/(a) are 0.00004 or less.

[0015] In the acrylamide system polymer of above-mentioned this invention, number average molecular weight (c) is 400,000-5,000,000, and it is desirable that weight-average-molecular-weight (a) and ratio [ of (c) ] (a)/(c) is six or less.

[0016] Polymer concentration is the range which is 22 - 60%, the Brookfield viscosity in 25 degrees C is below 50,000cps (centipoise), and this invention offers the acrylamide system polymer water solution whose weight average molecular weight is 500,000-10 million again.

[0017] Furthermore, this invention is [0018] expressed with the (a) (meta) acrylamide 94-99.98 mol % (b) cross-linking monomer 0.01 - one-mol % and (c) following general formula (1).

[Formula 5]



(The inside R1 of a formula is a hydrogen atom or the low-grade alkyl group of carbon numbers 1-3, and n is the integer of 1-4) The paper reinforcing agent which consists of a water-soluble polymer obtained [ make / into a constituent / 0.01-5 mol % of one sort or 2 sorts or more of vinyl compounds chosen from vinyl compounds and/or those salts ] by carrying out a polymerization is offered.

[0019] You may change to one sort or two sorts or more of vinyl compounds chosen from the vinyl compounds which copolymerizes [ the above-mentioned monomer of tales doses and ] 0.01 - 20-mol % and/or those salts of (a) as occasion demands.

[0020] the case where it is used as a paper reinforcing agent although the acrylamide system polymer in this invention says the copolymer which contains acrylamide and/or meta-acrylamide as the maximum component to all the monomer components that constitute the polymer formed from acrylamide and/or meta-acrylamide, or an acrylamide system polymer -- acrylamide and/or meta-acrylamide -- more than 50 mol % -- containing -- desirable -- further -- desirable -- 74-99.97-mol % -- it is 94-99.98-mol % especially preferably.

[0021] The weight average molecular weight (a) as used in the field of this invention can be calculated with static light scattering measurement. A value can be acquired by using the light-scattering detection equipment of whenever [ multiple ], and specifically creating a Zimm plot etc. Or it can obtain by creating a debye plot etc. by the GPC-MALLS method which connected the light-scattering detector to GPC whenever [ multiple ].

[0022] moreover, a weighted mean radius of inertia (b) -- above-mentioned GPC-MALLS -- it is measured by law.

[0023] Generally in the determination of molecular weight by light scattering measurement Basic type  $Kc/R$  of the following light scattering  $(\theta) = 1 - /MwP(\theta) + 2A_2 c + \dots$  the reduction on-the-strength  $c$  = sample concentration  $Mw$  = weight average molecular weight of the scattered light (Rayleigh multiplier) in the  $R(\theta)$  = include angle  $\theta$ , although an  $A_2 = 2\text{nd}$  virial coefficient  $K$  = optical parameter  $P(\theta)$  = include-angle scattering function is used GPC-MALLS as used in the field of this invention by which weight average molecular weight (a) connected the low include-angle light-scattering detector to GPC -- the value which disregarded like law the 2nd term or subsequent ones which is the 2nd virial coefficient shall be said

[0024] moreover, the weighted mean radius of inertia (b) as used in the field of this invention -- the root average of a weighted mean -- square -- the thing of a radius of inertia (Root Mean Square Radius -- generally shown by  $\langle S^2 \rangle^{1/2}$ ) is said.

[0025] In order to get to know the average degree of cross linking of a polymer, it becomes important to get to know the relation between weight average molecular weight and molecule sizes (radius of inertia etc.). Generally, it is known that what has the larger branching degree of cross linking of a polymer is smaller as for the molecule size of the polymer in the same presentation and the same molecular weight. Therefore, ratio [ of both at the time of specifying the range of the weight average molecular weight (a) in an acrylamide system polymer and a weighted mean radius of inertia (b) ]  $(b)/(a)$  can be used as an index which shows an average degree of cross linking.

[0026] As for the weight average molecular weight (a) of the acrylamide system polymer in this invention, 30 - 150nm and  $(b)/(a)$  of 1,500,000-10,000,000, and a weighted mean radius of inertia (b) is 0.00004 or less. When it takes into consideration that it is desirable that the polymer is equipped with the uniform branching structure of cross linkage, preferably, weight average molecular weight (a) is 2,000,000-8,000,000, a weighted mean radius of inertia (b) is 40-120nm, and  $(b)/(a)$  is 0.000035 or less.

[0027] When it takes into consideration that 400,000-5,000,000 have the desirable number average molecular weight (c) of the acrylamide system polymer in this invention, and it is desirable that it is equipped with the branching structure of cross linkage with a uniform polymer although six or less are desirable as for weight-average-molecular-weight (a) and ratio [ of (c) ]

(a)/(c), still more preferably, number average molecular weight (c) is 500,000-3,000,000, and (a)/(c) is four or less. in addition, the above-mentioned number average molecular weight (c) -- absolutely -- the thing of number average molecular weight -- it is -- GPC-MALLS -- it is measurable by law. Ratio [ of weight average molecular weight (a) and number average molecular weight (c) ] (a)/(c) shows the molecular weight distribution of a polymer.

[0028] In the acrylamide system polymer of this invention, although it has 1,000,000 or more molecular weight, when it takes into consideration that 40 % of the weight or more of a rate is desirable, and it is desirable that the polymer is equipped with the uniform branching structure of cross linkage, it is 50 % of the weight or more more preferably, and is 60 % of the weight or more still more preferably. the molecular weight in this case -- GPC-MALLS -- the absolute molecular weight measured by law -- saying -- GPC-MALLS -- it can know from the distribution curve of the absolute molecular weight by law.

[0029] Values, such as molecular weight of the polymer by the above light scattering measurement and a radius of inertia, can measure N / 15 phosphate buffer solutions containing N / 10 sodium nitrates (pH7) as a solvent (eluate).

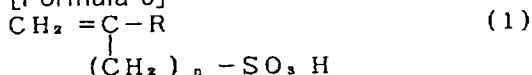
[0030] In the acrylamide system polymer of this invention, the diameter of hydration by dynamic light scattering is 50-300nm preferably, and is 70-300nm still more preferably. The diameter of hydration by dynamic light scattering says the hydrodynamic diameter by the Einstein-Stokes formula, uses N / 15 phosphate buffer solutions containing N / 10 sodium nitrates (pH7) as a solvent (eluate), and the value (temperature of 20 degrees C) measured by 90 degrees of diffusion angles by 0.1% of polymer concentration is said. Specifically, it can measure with equipments, such as N4 mold submicron particle analysis apparatus of a coal tar company. Data analysis is based on the SDP analysis which used Program CONTIN with the above-mentioned equipment.

[0031] It is 300 to 20,000 centipoise / 25 degrees C that the Brookfield viscosity [ in / in the Brookfield viscosity in 10% water-solution concentration of the acrylamide system polymer of this invention / 20 to 10,000 centipoise / 25 degrees C, or 15% water-solution concentration ] is 100 to 30,000 centipoise / 25 degrees C desirable still more preferably.

[0032] As an example of the acrylamide system polymer of this invention, one sort or the acrylamide system polymer obtained by copolymerizing two or more sorts is mentioned in the compounds shown, for example by acrylamide or meta-acrylamide, and the following general formula (1), or those salts.

[0033]

[Formula 6]



(For the inside R of a formula, a hydrogen atom or a low-grade alkyl group, and n are the integer of 1-8)

In a general formula (1), a low-grade alkyl group is an alkyl group of carbon numbers 1-3 preferably, and are specifically a methyl group, an ethyl group, n-propyl group, and an i-propyl group. The salt is alkali-metal salts, such as sodium and a potassium, ammonium salt, etc. It is expressed with a general formula (1) and an allyl compound sulfonic acid, sodium allylsulfonate, a metallyl sulfonic acid, sodium methallylsulfonate, metallyl sulfonate ammonium, etc. can be illustrated as an example of a sulfonic-acid-ized compound, for example.

[0034] It is 0.05-10-mol % preferably [ it is desirable and ] to 0.01-20-mol % and a pan from it being desirable that the polymer is equipped with the uniform branching structure of cross linkage as an amount of these compounds to the total amount of all the monomers that constitute an acrylamide system polymer although it is 0.005-30-mol %. Moreover, when [ 0.01-5 mol% of ] using it as an internal form force enhancement agent, it is desirable, and 0.05-5-mol % is the most desirable. these compounds -- a kind -- or two or more sorts can be used, using together.

[0035] In addition, the effectiveness as a regulator of acrylamide is indicated by the U.S. Pat. No. 4451628 number about a metallyl sulfonic acid and its salt. However, this approach shows that



the acrylamide system polymer of low molecular weight is obtained, and the polymers which controlled branching and the structure of cross linkage of this invention completely differ in the polymer obtained.

[0036] Furthermore, in addition to the compound shown by the general formula (1), the acrylamide system polymer of this invention can be more easily obtained by using a cross-linking monomer.

[0037] When this cross-linking monomer is listed concretely, methylenebis acrylamide, Methylenebis meta-acrylamide, ethylene bis-acrylamide, ethylene bis-meta acrylamide, Ethylene glycol diacrylate, ethylene glycol dimethacrylate, Diethylene glycol diacrylate, diethylene glycol dimethacrylate, Two organic-functions mold cross-linking monomers, such as triethylene glycol diacrylate, triethylene glycol dimethacrylate, a divinylbenzene, and diaryl acrylamide, Or 1, 3, 5-thoria chestnut roil hexahydro-S-triazine, Polyfunctional mold cross-linking monomers, such as triallyl isocyanurate, thoria krill acid pentaerythritol, trimethylol propane acrylate, triacrylformal, and diacryloyl imide, can be illustrated. As an amount of these cross-linking monomers, it is desirable that it is 0.005-5-mol % to the total amount of all the monomers that constitute an acrylamide system polymer. Since it is desirable that the polymer is equipped with the uniform branching structure of cross linkage, it is still more desirable that it is [ 0.01-2 mol ] %, and especially 0.01-1-mol % is desirable. these compounds -- one sort -- or two or more sorts can be used, using together.

[0038] The acrylamide system polymer in this invention can be manufactured also by carrying out copolymerization more than of one sort or it of various vinyl monomers in addition to acrylamide and/or methacrylamide. An ionicity monomer, a hydrophilic monomer, a hydrophobic monomer, etc. are raised to them.

[0039] As an anionic monomer, unsaturated carboxylic acid, such as an acrylic acid, a methacrylic acid, an itaconic acid, a maleic acid, and a fumaric acid, and those salts, a vinyl sulfonic acid, a styrene sulfonic acid, acrylamide methyl propane sulfonic acids, and those salts are mentioned among ionicity monomers, for example.

[0040] As a cationic monomer, amines, those salts (the 4th class ghost is also included), etc., such as N and N-dimethylaminoethyl methacrylate, N, and N-diethylamino ethyl methacrylate, N, and N-dimethylamino ethyl acrylate, N-N-dimethylaminopropyl methacrylamide, and N,N-dimethylaminopropyl acrylamide, can be raised.

[0041] As a hydrophilic monomer, for example Acetone acrylamide, N,N-dimethylacrylamide, N and N-dimethyl methacrylamide, N-ethyl methacrylamide, N-ethyl acrylamide, N, and N-diethyl acrylamide, N-propyl acrylamide, N-acryloyl pyrrolidine, N-acryloyl piperidine, N-acryloyl morpholine, Hydroxyethyl methacrylate, hydroxyethyl acrylate, hydroxypropyl methacrylate, hydroxypropyl acrylate, various kinds of methoxy polyethylene-glycol (meta) acrylate, an N-vinyl-2-pyrrolidone, etc. can be raised.

[0042] As a hydrophobic monomer, for example N and N-G n-propyl acrylamide, N-n-butyl acrylamide, N-n-hexyl acrylamide, N-n-hexyl methacrylamide, N-n-octyl acrylamide, N-n-octyl methacrylamide, N-tert-octyl acrylamide, N-alkyl (meta) acrylamide derivatives, such as N-dodecyl acrylamide and N-n-dodecyl methacrylamide, N and N-diglycidyl acrylamide, N, and N-diglycidyl methacrylamide, N-(4-glycidoxybutyl) acrylamide, N-(4-glycidoxybutyl) methacrylamide, N-(omega-glycidoxy alkyl) (meta) acrylamide derivatives, such as N-(5-glycidoxy pentyl) acrylamide and N-(6-glycidoxy hexyl) acrylamide, Methyl (meta) acrylate, ethyl (meta) acrylate, butyl (meta) acrylate, Lauryl (meta) acrylate, 2-ethylhexyl (meta) acrylate, Acrylate (meta) derivatives, such as glycidyl (meta) acrylate, Olefins, such as acrylonitrile, a methacrylonitrile, vinyl acetate, a vinyl chloride, a vinylidene chloride, ethylene, a propylene, and a butene, styrene, alpha methyl styrene, a butadiene, an isoprene, etc. can be raised.

[0043] The amount of the vinyl monomer used with which copolymerization is presented changes with the classes of vinyl monomer, and those combination, and although there is no \*\*\*\*\* generally, it is in the 0-50-mol range of % in general. the case where an acrylamide system polymer is used as a paper reinforcing agent -- an anionic polymer -- desirable -- 0-20-mol % -- it is more preferably used at 0.5-10-mol % -- having -- and a cationic polymer -- desirable -- 0-20-mol % -- it is more preferably [ 0.5-10 mol% of ] the optimal.

[0044] this invention -- following -- concentration -- the water solution of the acrylamide polymer of 500,000-10,000,000 is offered [ the Brookfield viscosity in 25 degrees C ] for weight average molecular weight by 50,000cps or less in 30-60% of range especially 22 to 60%. The concentration and molecular weight of the range which does not have trouble in a paper reinforcing agent application, for example are 500,000-3 million by 500,000 - 4 million or 50% concentration in 500,000 - 6 million or 40% concentration with 500,000 - 8 million or 30% concentration in general from the desirable homogeneous point of the branching structure of cross linkage at 25% concentration.

[0045] In addition, polymer concentration can be obtained by measuring the bone-dry polymer concentration of a polymer water solution. As a measuring method, a hot-air-drying method, the blanket method, etc. are mentioned.

[0046] As a polymerization method of the acrylamide system polymer in this invention, a radical polymerization is desirable. Although polar solvents, such as water, alcohol, and dimethylformamide, are applicable as a polymerization solvent, when using it as a paper reinforcing agent, it is desirable that it is aqueous polymerization. In the case of aqueous polymerization, it is possible to carry out concomitant use with organic solvents, such as alcohol, in the range in which a polymer carries out deposit sedimentation and does not spoil dispersibility.

[0047] The batch (batch) polymerization which teaches all monomers to a reaction container by package, and carries out a polymerization is sufficient as the polymerization method of the acrylamide system polymer in this invention. \*\* et al. [ however, ] -- when obtaining 22% or more of high concentration water solution, while especially a part or all of a monomer is dropped into a reaction container, it is more desirable that it is the half-batch (semi batch) polymerization method which carries out a polymerization. It not only becomes easy to remove the heat of polymerization in monomer high concentration liquid, but by performing a semi batch polymerization method, equalization of the branching structure of cross linkage of a polymer becomes controllable [ becoming easy etc. / the molecular structure ].

[0048] Especially a limit does not have the polymerization concentration shown by the monomer + polymer concentration at the time of a polymerization, and two to 40% of the weight, although it is 5 - 40 % of the weight preferably, in case 22% of the weight or more of a high concentration water solution is obtained, it is usually as follows.

[0049] That is, the polymerization concentration in the case of batch polymerization is 22 - 40 % of the weight in general. Although a polymerization is carried out by concentration lower than 22 % of the weight and the obtained polymerization reaction mixture is not interfered by concentration actuation as a polymer water solution of 22% of the weight or more of concentration, it is disadvantageous in respect of economical efficiency. In the case of semi batch polymerization, the polymerization concentration in the reactor under dropping can be chosen at arbitration by adjusting the initial monomer concentration in a reactor, and the dropping rate of a monomer. However, the polymerization concentration at the time of dropping termination is 22 - 60 % of the weight in general. In this case, there is a disadvantageous point which carried out [ a point ] the polymerization by concentration lower than 22 % of the weight, and was mentioned above by concentration actuation like batch polymerization although it was also possible to have considered as the polymer water solution of 22% of the weight or more of concentration.

[0050] Although there is nothing, if especially a limit of a polymerization initiator is a water-soluble thing, it is desirable. You may add collectively in a monomer water solution, and it may be dropped. As a concrete polymerization initiator, ammonium persulfate, potassium persulfate, sodium persulfate, a hydrogen peroxide, a benzoyl peroxide, tert-butyl peroxide, etc. are mentioned by the persulfate system and the peroxide system, for example. In this case, although it is more desirable to use it independently, it can be used also as a redox system polymerization initiator combining a reducing agent. As a reducing agent, reducing sugars, such as organic amines, such as salts of ionization of a low degree, such as a sulfite, a hydrogensulfite, iron, copper, and cobalt salt, N and N, N', and N'-tetramethyl ethylene diamine, and also an aldose, and a ketose, etc. can be mentioned, for example.

[0051] An azo compound is also the most desirable initiator in this invention. A 2 and 2'-azobis-2-methyl propione amidine hydrochloride, A 2 and 2'-azobis-2,4-dimethylvaleronitrile, 2, and 2'-azobis-N and N'-dimethylene isobutyl amidine hydrochloride, 2 and 2'-azobis-2-methyl-N -(2-hydroxyethyl)- Propione amide, 2, and 2'-azobis -2 -(2-imidazoline-2-IRU)- A propane and its salt, 4, and 4'-azobis-4-cyano valeric acid, its salt, etc. can be used. Furthermore, it is also possible to use together two or more sorts of above-mentioned polymerization initiators. The amount of a polymerization initiator is 0.001 - 5 % of the weight to a monomer in general.

[0052] In the case of a single polymerization initiator, polymerization temperature is 30-90 degrees C in general, and the initiation temperature in the case of a redox system polymerization initiator is 5-50 degrees C in general lower. Moreover, although it is not necessary to maintain at same-during polymerization temperature and you may change suitably with advance of a polymerization, in order to carry out a temperature up by the heat of polymerization generally generated with advance of a polymerization, it may be necessary to add cooling if needed. It is better for inert gas like nitrogen gas to permute with making a polymerization perform promptly, although especially limitation does not have an ambient atmosphere in the polymerization container at that time. Although especially limitation does not have polymerization time amount, it is 1 - 20 hours in general also including the drop time in semi batch polymerization. Although especially limitation does not have Polymerization pH, pH adjustment may be carried out if needed and a polymerization may be performed. In that case, organic acids, such as mineral acids, such as alkalization agents, such as a sodium hydroxide, a potassium hydroxide, and ammonia, a phosphoric acid, a sulfuric acid, and a hydrochloric acid, formic acid, and an acetic acid, etc. are mentioned as an usable pH regulator.

[0053] The acrylamide system polymer which is not known at all conventionally as mentioned above and its water solution can be obtained, and the polymer and water solution which were obtained can demonstrate many effectiveness which was excellent as a paper reinforcing agent. The case where the acrylamide system polymer of this invention is used for below as a paper reinforcing agent is further explained to a detail.

[0054] It is with what is used for a paper reinforcing agent by adding in a pulp slurry (for internal), and the thing (for outside \*\*) used by applying or sinking into the paper sheet after wire dehydration, and the acrylamide system polymer of this invention can be used for the all.

[0055] The paper reinforcing agent by this invention is usually used by the following approaches. That is, when used as an object for internal, in a pulp slurry, it uses together with fixing agents, such as a sulfuric-acid band, and is added if needed. The amount of the paper reinforcing agent used in this case (solid content) is 0.05 - 3% to pulp solid content in general. moreover, the same as the above by size press, calender spreading, etc., when using it as an object for outside \*\* -- amount use is carried out.

[0056] When using the acrylamide system polymer water solution more than 22% concentration as a paper reinforcing agent, weight average molecular weight should just be 500,000-10 million. Although desirable one has the economically undoubted one where polymer concentration is higher, viscosity is good [ in it being below 20,000cps (centipoise) still more preferably ] at the time of circulation preferably below 50,000cps (centipoise) below 30,000cps (centipoise) from the point of the workability at the time of use.

[0057] In addition, a polymer water solution is used, diluting it suitably.

[0058] By the approach of this invention, the acrylamide system polymer of such new structure nature and its water solution come to be obtained by what kind of reason, or, at present, it is unknown. When the polymer to which the compound shown by general formulas 1 or 2 reacted reacts specifically with the radical in a polymerization and other polymers, or the pendant double bond of a cross-linking monomer reason, branching bridge formation advances efficiently and it is imagined as that from which the acrylamide system polymer which has the much more uniform branching structure of cross linkage is obtained as compared with what is known conventionally as a result. furthermore, since this polymer has the uniform branching structure of cross linkage, it increases the pasting up point between pulp fiber indirectly -- making -- the former -- furthermore, it is thought as an outstanding paper reinforcing agent that various engine performance is demonstrated.

[0059]

[Example] Below, an example explains this invention concretely. In addition, this invention is not limited to these examples. Moreover, especially the thing shown by % below shall mean weight %, unless it refuses.

[0060] The Measuring condition of GPC-MALLS in an example is as follows.

[0061] GPC body: The Showa Denko K.K. make, system 11 column:SHODEX SB 80M eluate: N / 15 phosphate buffer solutions containing N / 10 sodium nitrates (pH7)

rate-of-flow: -- a part for 1.0ml/-- detector: -- the internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into light-scattering detector DAWN example 1 stirrer, a reflux cooling pipe, a thermometer, nitrogen gas installation tubing, and 5 opening flask (it is hereafter called a reaction container) equipped with dropping opening for 500g of pure water whenever [ multiple / of the Wyatt technology company ].

[0062] 60g of water solutions which, on the other hand, dissolved 0.18g of 4 and 4'-azobis-4-cyano valeric acids of the solution which carried out the mixed dissolution of 354.3g [ of acrylamide water solutions ] and methylenebis acrylamide 0.308g and the 0.632g of the sodium methallylsulfonate 40%, and 84% of pure parts was adjusted, it applied for 130 minutes into the reaction container, respectively, and equal dropping was carried out. In the meantime, the temperature in a reaction container was kept at 80 degrees C. The acrylamide system polymer water solution with the nonvolatile matter of 15%, the Brookfield viscosity of 18000cps in 25 degrees C, 10% [ of nonvolatile matters ], and a Brookfield viscosity [ in 25 degrees C ] of 1780cps was obtained after dropping termination by continuing a polymerization for 3 hours, adding water, cooling further, and terminating a reaction at 80 degrees C. This polymer is set to A-1. the weight average molecular weight (a) of A-1, and a weighted mean radius of inertia (b) -- GPC-MALLS -- when measured by law, it was 3050000 or 73.8nm and was (b)/(a) = 0.0000242, respectively. Moreover, more absolutely than the law, number average molecular weight (c) was 1250000, and was (a)/(c) = 2.44. Furthermore, it was 73.5% when asked for the with a molecular weight of 1 million or more weight rate (d) from the distribution curve. On the other hand, it was 120nm when asked for the diameter of hydration (e) by N4 mold submicron particle analysis apparatus by the coal tar company.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 2 aforementioned reaction container for 560g of pure water.

[0063] On the other hand, the mixed dissolution of the 0.9g of the 4 and 4'-azobis-4-cyano valeric acids of 354.1g [ of 40% acrylamide water solutions ] and methylenebis acrylamide 1.23g, 0.79g of sodium methallylsulfonate, and 84% of pure parts was carried out, and monomer initiator mixed liquor was adjusted.

[0064] Then, equal dropping was carried out, having monomer initiator applied [ this ] it for 150 minutes into the reaction container. In the meantime, the temperature in a reaction container was kept at 80 degrees C. Moreover, the temperature of monomer initiator mixed liquor is kept at 20 degrees C or less, and it was made for a polymerization not to produce it before dropping.

[0065] The acrylamide system polymer water solution with the nonvolatile matter of 15%, the Brookfield viscosity of 2170cps in 25 degrees C, 10% [ of nonvolatile matters ], and a Brookfield viscosity [ in 25 degrees C ] of 330cps was obtained after dropping termination by continuing a polymerization for 3 hours, adding water, cooling further, and terminating a reaction at 80 degrees C. This polymer is set to A-2. Many physical-properties values of A-2 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 3 aforementioned reaction container for 257.5g of pure water.

[0066] On the other hand, the solution which carried out the mixed dissolution of 532.6g [ of acrylamide water solutions ] and methylenebis acrylamide 0.585g and the 7.865g of the sodium methallylsulfonate 50%, and 60g of water solutions which dissolved NaOH of 0.38g of 4 and 4'-azobis-4-cyano valeric acids of 84% of pure parts, and it and 2 double mol were adjusted further, it applied for 150 minutes into the reaction container, respectively, and equal dropping was carried out. In the meantime, the temperature in a reaction container was kept at 80 degrees C.

[0067] The acrylamide system polymer water solution with the nonvolatile matter of 15%, the

Brookfield viscosity of 630cps in 25 degrees C, 10% [ of nonvolatile matters ], and a Brookfield viscosity [ in 25 degrees C ] of 170cps was obtained after dropping termination by continuing a polymerization for 3 hours, adding water, cooling further, and terminating a reaction at 80 degrees C. This polymer is set to A-3. Many physical-properties values of A-3 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 4 aforementioned reaction container for 177.0g of pure water.

[0068] On the other hand, the mixed dissolution of the 0.544g of the 4 and 4'-azobis-4-cyano valeric acids of 750.7g [ of 50% acrylamide water solutions ] and methylenebis acrylamide 0.837g, 23.8g of sodium methallylsulfonate, and 84% of pure parts was carried out, and monomer initiator mixed liquor was adjusted.

[0069] Then, equal dropping was carried out, having monomer initiator applied [ this ] it for 150 minutes into the reaction container. In the meantime, the temperature in a reaction container was kept at 80 degrees C. Moreover, the temperature of monomer initiator mixed liquor is kept at 20 degrees C or less, and it was made for a polymerization not to produce it before dropping.

[0070] The acrylamide system polymer water solution with the nonvolatile matter of 15%, the Brookfield viscosity of 550cps in 25 degrees C, 10% [ of nonvolatile matters ], and a Brookfield viscosity [ in 25 degrees C ] of 150cps was obtained after dropping termination by continuing a polymerization for 3 hours, adding water, cooling further, and terminating a reaction at 80 degrees C. This polymer is set to A-4. Many physical-properties values of A-4 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 5 aforementioned reaction container for 395.8g of pure water.

[0071] On the other hand, the mixed dissolution of the 0.9g of the 4 and 4'-azobis-4-cyano valeric acids of 339.4g [ of 40% acrylamide water solutions ] and methylenebis acrylamide 4.62g, 9.48g of sodium methallylsulfonate, and 84% of pure parts was carried out, and monomer initiator mixed liquor was adjusted.

[0072] Then, equal dropping was carried out, having monomer initiator applied [ this ] it for 150 minutes into the reaction container. In the meantime, the temperature in a reaction container was kept at 80 degrees C. Moreover, the temperature of monomer initiator mixed liquor is kept at 20 degrees C or less, and it was made for a polymerization not to produce it before dropping.

[0073] The acrylamide system polymer water solution with the nonvolatile matter of 15%, the Brookfield viscosity of 106cps in 25 degrees C, 10% [ of nonvolatile matters ], and a Brookfield viscosity [ in 25 degrees C ] of 38cps was obtained after dropping termination by continuing a polymerization for 3 hours, adding water, cooling further, and terminating a reaction at 80 degrees C. This polymer is set to A-5. Many physical-properties values of A-5 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example of comparison 1 aforementioned reaction container for 500g of pure water.

[0074] On the other hand, 0.9g of the 4 and 4'-azobis-4-cyano valeric acid of 84% of pure parts was dissolved in 355.4g of acrylamide water solutions 40%, and the monomer initiator mixed liquor which added 60g of water was adjusted.

[0075] Then, equal dropping was carried out, having monomer initiator applied [ this ] it for 150 minutes into the reaction container. In the meantime, the temperature in a reaction container was kept at 80 degrees C. Moreover, the temperature of monomer initiator mixed liquor is kept at 20 degrees C or less, and it was made for a polymerization not to produce it before dropping.

[0076] The acrylamide system polymer water solution with the nonvolatile matter of 15%, the Brookfield viscosity of 30000cps in 25 degrees C, 10% [ of nonvolatile matters ], and a Brookfield viscosity [ in 25 degrees C ] of 2820cps was obtained after dropping termination by continuing a polymerization for 3 hours, adding water, cooling further, and terminating a reaction at 80 degrees C. This polymer is set to C-1. Many physical-properties values of C-1 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example of comparison 2 aforementioned reaction container for 500g of pure water.

[0077] Although 355.0g of 40% acrylamide water solutions, the solution which carried out the mixed dissolution of the methylenebis acrylamide 0.308g, and 60g of water solutions which dissolved 0.18g of the 4 and 4'-azobis-4-cyano valeric acid of 84% of pure parts were adjusted further on the other hand and equal dropping was carried out like the example 1 into the reaction container, respectively, it was in the middle of dropping, and the fluidity of reaction mixture was lost and it gelled. This gelation polymer is set to C-2. Even if it diluted C-2 more than it, the distributed dissolution of it was not able to be carried out, and it was not able to measure many physical-properties values.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example of comparison 3 aforementioned reaction container for 500g of pure water.

[0078] On the other hand, 0.9g of the 4 and 4'-azobis-4-cyano valeric acid of 355.0g [ of 40% acrylamide water solutions ] and methylenebis acrylamide 0.308g and 84% of pure parts was dissolved, and the monomer initiator mixed liquor which added 60g of water was adjusted.

[0079] Then, equal dropping was carried out, having monomer initiator applied [ this ] it for 150 minutes into the reaction container. In the meantime, the temperature in a reaction container was kept at 80 degrees C. Moreover, the temperature of monomer initiator mixed liquor is kept at 20 degrees C or less, and it was made for a polymerization not to arise before dropping.

[0080] The acrylamide system polymer water solution with the nonvolatile matter of 15%, the Brookfield viscosity of 15000cps in 25 degrees C, 10% [ of nonvolatile matters ], and a Brookfield viscosity [ in 25 degrees C ] of 1400cps was obtained after dropping termination by continuing a polymerization for 3 hours, adding water, cooling further, and terminating a reaction at 80 degrees C. This polymer is set to C-3. Many physical-properties values of C-3 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example of comparison 4 aforementioned reaction container for 395.8g of pure water.

[0081] On the other hand, although the mixed dissolution was carried out and equal dropping of the 0.9g of the 4 and 4'-azobis-4-cyano valeric acid of 348.3g [ of 40% acrylamide water solutions ] and methylenebis acrylamide 4.62g and 84% of pure parts was carried out like the example 4 into the reaction container, it was in the middle of dropping, and the fluidity of reaction mixture was lost and it gelled. This gelation polymer is set to C-4. Even if it diluted C-4 more than it, the distributed dissolution of it was not able to be carried out, and it was not able to measure many physical-properties values.

[0082] The polymer A-1 to A-5, the presentation of C-1 to C-4, and many physical-properties values which were acquired in examples 1-5 and the examples 1-4 of a comparison were collectively shown in Table 1 and 2 [Tables 1 and 2].

[0083]

[Table 1]

	組成 (モル%)			1) 重合開始剤 (g/モル)	ポリマーNo
	AM	SMS	MBA		
実施例 1	99.7	0.2	0.1	0.09	A-1
実施例 2	99.35	0.25	0.4	0.45	A-2
実施例 3	98.6	1.3	0.1	0.10	A-3
実施例 4	97.13	2.77	0.1	0.10	A-4
実施例 5	95.5	3.0	1.5	0.45	A-5
比較例 1	100			0.45	C-1
比較例 2	99.9		0.1	0.09	C-2
比較例 3	99.9		0.1	0.45	C-3
比較例 4	98.5		1.5	0.45	C-4

AM: アクリルアミド、

SMS: メタリルスルホン酸ナトリウム、

MBA: メチレンビスアクリルアミド、

1) 4, 4'-アゾビス-4-シアノ吉草酸

[0084]

[Table 2]

ポリマー	15% 製品 (cps /25℃)	10% 製品 (cps /25℃)	重量平均 分子量 (a) (万)	重量平均 慣性半径 (b) (nm)	(b) —— (a)	数平均 分子量 (c) (万)	(a) —— (c)	分子量 100 万 以上 (%)	水和径 (nm)
A-1	18000	1780	305	73.8	0.0000242	125	2.44	73.5	120
A-2	2170	330	339	80.2	0.0000237	88.0	3.85	74.0	170
A-3	630	170	312	72.2	0.0000231	113	2.76	71.8	240
A-4	550	150	315	77.0	0.0000244	105	3.00	66.7	170
A-5	106	38	206	61.5	0.0000299	51.3	4.02	41.4	93
C-1	30000	2820	69.4	35.2	0.0000507	32.2	2.16	18.9	37
C-2	ゲル化								
C-3	15000	1400	64.9	30.1	0.0000464	27.8	2.33	18.4	28
C-4	ゲル化								

C-1 および C-3 の水和径は、コールター N4 の散乱強度 (カウンタ数) が 50000 以下であり、本来測定できないが、散乱強度 50000 以下における参考値を示す。

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 6 aforementioned reaction container for 600g of pure water.

[0085] On the other hand, the mixed dissolution of 332.8g [ of 40% acrylamide water solutions ] and methylenebis acrylamide 0.308g, 0.79g [ of sodium methallylsulfonate ], N, and N-dimethylaminoethyl METARI rate 12.6g and the 5.2g of the itaconic acids was carried out, and pH was adjusted to 4.2 by HCl 35%.

[0086] Moreover, 60g of water solutions which dissolved 0.16g of 4 and 4'-azobis-4-cyano valeric acids of 84% of pure parts was adjusted.

[0087] Next, equal dropping was carried out, having poured [ above-mentioned / both ] it for 150 minutes into the reaction container, respectively. In the meantime, the temperature in a reaction container was kept at 80 degrees C.

[0088] The acrylamide system polymer water solution with the nonvolatile matter of 15%, the Brookfield viscosity of 5000cps in 25 degrees C, 10% [ of nonvolatile matters ], and a Brookfield viscosity [ in 25 degrees C ] of 960cps was obtained after dropping termination by adding water and adjusting a nonvolatile matter at 80 degrees C, while continuing a polymerization for 3 hours,

cooling and terminating a reaction. This polymer is set to A-6. Many physical-properties values of A-6 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 7 aforementioned reaction container for 660g of pure water.

[0089] On the other hand, the mixed dissolution of the 0.9g of the 4 and 4'-azobis-4-cyano valeric acids of 331.8g [ of 40% acrylamide water solutions ] and methylenebis acrylamide 1.23g, 0.79g [ of sodium methallylsulfonate ], N, and N-dimethylaminoethyl METARI rate 12.6g, 5.2g of itaconic acids, and 84% of pure parts was carried out, pH adjustment was carried out by HCl 35%, and the monomer initiator mixed liquor of pH4.2 was obtained.

[0090] Next, equal dropping was carried out, having monomer initiator applied [ above-mentioned ] it for 150 minutes into the reaction container. In the meantime, the temperature in a reaction container was kept at 80 degrees C. Moreover, the temperature of monomer initiator mixed liquor is kept at 20 degrees C or less, and it was made for a polymerization not to arise before dropping.

[0091] The acrylamide system polymer water solution with the nonvolatile matter of 15%, the Brookfield viscosity of 3000cps in 25 degrees C, 10% [ of nonvolatile matters ], and a Brookfield viscosity [ in 25 degrees C ] of 620cps was obtained after dropping termination by adding water and adjusting a nonvolatile matter at 80 degrees C, while continuing a polymerization for 3 hours, cooling and terminating a reaction. This polymer is set to A-7. Many physical-properties values of A-7 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 8 aforementioned reaction container for 580g of pure water.

[0092] On the other hand, the mixed dissolution of 325.7g [ of 40% acrylamide water solutions ] and methylenebis acrylamide 0.308g, 0.79g of sodium methallylsulfonate, 12.5g of N,N-dimethylaminopropyl acrylamide, and the 7.2g of the 80% acrylic acids was carried out, and pH was adjusted to 4.2 by HCl 35%.

[0093] Moreover, 60g of water solutions which dissolved 0.16g of 4 and 4'-azobis-4-cyano valeric acids of 84% of pure parts was adjusted.

[0094] Next, equal dropping was carried out, having poured [ above-mentioned / both ] it for 150 minutes into the reaction container, respectively. In the meantime, the temperature in a reaction container was kept at 80 degrees C.

[0095] The acrylamide system polymer water solution with the nonvolatile matter of 15%, the Brookfield viscosity of 11000cps in 25 degrees C, 10% [ of nonvolatile matters ], and a Brookfield viscosity [ in 25 degrees C ] of 1980cps was obtained after dropping termination by adding water and adjusting a nonvolatile matter at 80 degrees C, while continuing a polymerization for 3 hours, cooling and terminating a reaction. This polymer is set to A-8. Many physical-properties values of A-8 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 9 aforementioned reaction container for 387g of pure water.

[0096] On the other hand, the mixed dissolution of 414.6g [ of 40% acrylamide water solutions ] and methylenebis acrylamide 0.385g, 2.25g [ of sodium methallylsulfonate ], N, and N-dimethylaminoethyl methacrylate 15.7g and the 6.5g of the itaconic acids was carried out, and pH was adjusted to 4.2 by HCl 35%.

[0097] Moreover, 60g of water solutions which dissolved NaOH of 0.25g of 4 and 4'-azobis-4-cyano valeric acids of 84% of pure parts, and it and 2 double mol was adjusted.

[0098] Next, equal dropping was carried out, having poured [ above-mentioned / both ] it for 150 minutes into the reaction container, respectively. In the meantime, the temperature in a reaction container was kept at 80 degrees C.

[0099] The acrylamide system polymer water solution with the nonvolatile matter of 15%, the Brookfield viscosity of 1500cps in 25 degrees C, 10% [ of nonvolatile matters ], and a Brookfield viscosity [ in 25 degrees C ] of 340cps was obtained after dropping termination by adding water and adjusting a nonvolatile matter at 80 degrees C, while continuing a polymerization for 3 hours, cooling and terminating a reaction. This polymer is set to A-9. Many physical-properties values of A-9 were measured like the example 1.



The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example of comparison 5 aforementioned reaction container for 660g of pure water.

[0100] On the other hand, the mixed dissolution of the 0.9g of the 4 and 4'-azobis-4-cyano valeric acids of 333.7g [ of 40% acrylamide water solutions ] and methylenebis acrylamide 0.308g, N, and N-dimethylaminoethyl METARI rate 12.6g, 5.2g of itaconic acids, and 84% of pure parts was carried out, and pH was adjusted to 4.2 by HCl 35%.

[0101] Next, equal dropping was carried out, having poured [ above-mentioned ] it for 150 minutes into the reaction container. In the meantime, the temperature in a reaction container was kept at 80 degrees C.

[0102] The acrylamide system polymer water solution with the nonvolatile matter of 15%, the Brookfield viscosity of 9200cps in 25 degrees C, 10% [ of nonvolatile matters ], and a Brookfield viscosity [ in 25 degrees C ] of 630cps was obtained after dropping termination by adding water and adjusting a nonvolatile matter at 80 degrees C, while continuing a polymerization for 3 hours, cooling and terminating a reaction. This polymer is set to C-5. Many physical-properties values of C-5 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example of comparison 6 aforementioned reaction container for 600g of pure water.

[0103] On the other hand, the mixed dissolution of 333.7g [ of 40% acrylamide water solutions ] and methylenebis acrylamide 0.308g, N, and N-dimethylaminoethyl METARI rate 12.6g and the 5.2g of the itaconic acids was carried out, and pH was adjusted to 4.2 by HCl 35%.

[0104] Moreover, 60g of water solutions which dissolved 0.16g of 4 and 4'-azobis-4-cyano valeric acids of 84% of pure parts was adjusted.

[0105] Next, although equal dropping of both the above-mentioned water solutions was carried out like the example 6 into the reaction container, respectively, it was in the middle of dropping, and the fluidity of reaction mixture was lost and it gelled. This gelation polymer is set to C-6. Even if it diluted C-6 more than it, the distributed dissolution of it was not able to be carried out, and it was not able to measure many physical-properties values.

The mixed dissolution of 333.7g [ of 40% acrylamide water solutions ] and methylenebis acrylamide 0.308g, N, and N-dimethylaminoethyl METARI rate 12.6g, 5.2g of itaconic acids, and the 660g of the water was carried out, and pH was adjusted to the example of comparison 7 aforementioned reaction container by HCl 35% 4.2.

[0106] Next, it is the above-mentioned mixed liquor in a reaction container N2 The reaction container was kept warm, after deoxidizing by gas and carrying out the temperature up of the solution temperature to 45 degrees C.

[0107] Subsequently, stirring, 1.32g of ammonium persulfates and 0.6g of sodium hydrogensulfites were added, and the polymerization was made to start. Solution temperature amounted to 80 degrees C after 60 minutes, and it was left at 80 degrees C after that for 1 hour. Then, while cooling and terminating the reaction, the acrylamide system polymer water solution with the nonvolatile matter of 15%, the Brookfield viscosity of 8700cps in 25 degrees C, 10% [ of nonvolatile matters ], and a Brookfield viscosity [ in 25 degrees C ] of 1700cps was obtained by adding water and adjusting a nonvolatile matter. This polymer is set to C-7. Many physical-properties values of C-7 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example of comparison 8 aforementioned reaction container for 660g of pure water.

[0108] On the other hand, the mixed dissolution of the 0.9g of the 4 and 4'-azobis-4-cyano valeric acids of 332.7g [ of 40% acrylamide water solutions ] and methylenebis acrylamide 1.23g, N, and N-dimethylaminoethyl METARI rate 12.6g, 5.2g of itaconic acids, and 84% of pure parts was carried out, and pH was adjusted to 4.2 by HCl 35%.

[0109] Next, although equal dropping of the above-mentioned water solution was carried out like the example 7 into the reaction container, it was in the middle of dropping, and the fluidity of reaction mixture was lost and it gelled. This gelation polymer is set to C-8. Even if it diluted C-8 more than it, the distributed dissolution of it was not able to be carried out, and it was not able to measure many physical-properties values.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the

example of comparison 9 aforementioned reaction container for 660g of pure water.

[0110] On the other hand, the mixed dissolution of the 0.9g of the 4 and 4'-azobis-4-cyano valeric acids of allyl alcohol 9.85g and 84% of pure parts was carried out as 332.7g [ of 40% acrylamide water solutions ], and methylenebis acrylamide 1.23g, N, and N-dimethylaminoethyl METARI rate 12.6g, 5.2g of itaconic acids, and a molecular-weight regulator, and pH was adjusted to 4.2 by HCl 35%.

[0111] Next, equal dropping was carried out, having poured [ above-mentioned ] it for 150 minutes into the reaction container. In the meantime, the temperature in a reaction container was kept at 80 degrees C.

[0112] The nonvolatile matter of 15%, the Brookfield viscosity of 10000cps in 25 degrees C, 10% of nonvolatile matters, and the acrylamide system polymer water solution of Brookfield viscosity [ of 1860cps ] \*\* in 25 degrees C were obtained after dropping termination by adding water and adjusting a nonvolatile matter at 80 degrees C, while continuing a polymerization for 3 hours, cooling and terminating a reaction. This polymer is set to C-9. Many physical-properties values of C-9 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example of comparison 10 aforementioned reaction container for 560g of pure water.

[0113] On the other hand, the mixed dissolution of the 325.7g [ of 40% acrylamide water solutions ] and methylenebis acrylamide 0.308g, 2.6g [ of 25% sodium vinylsulfonate water solutions ], 12.5g [ of N,N-dimethylaminopropyl acrylamide ], 7.2g [ of 80% acrylic acids ], and isopropyl alcohol 23g was carried out, and pH was adjusted to 4.2 by HCl 35%.

[0114] Moreover, 60g of water solutions which dissolved 0.16g of 4 and 4'-azobis-4-cyano valeric acids of 84% of pure parts was adjusted.

[0115] Next, equal dropping was carried out, having poured [ above-mentioned / both ] it for 150 minutes into the reaction container, respectively. In the meantime, the temperature in a reaction container was kept at 80 degrees C.

[0116] The nonvolatile matter of 15%, the Brookfield viscosity of 6800cps in 25 degrees C, 10% of nonvolatile matters, and the acrylamide system polymer water solution of Brookfield viscosity [ of 170cps ] \*\* in 25 degrees C were obtained after dropping termination by adding water and adjusting a nonvolatile matter at 80 degrees C, while continuing a polymerization for 3 hours, cooling and terminating a reaction. This polymer is set to C-10. Many physical-properties values of C-10 were measured like the example 1.

[0117] The polymer A-6 to A-9, the presentation of C-5 to C-10, and many physical-properties values which were acquired in examples 6-9 and the examples 5-10 of a comparison were collectively shown in Tables 3 and 4 [Tables 3 and 4].

[0118]

[Table 3]

	組 成 (モル%)						1) 重合開始剤 (g/モル)	ポリマー No
実施例 6	AM 93.7	DM 4	IA 2	SMS 0.25	MBA 0.1		0.08	A-6
実施例 7	AM 93.35	DM 4	IA 2	SMS 0.25	MBA 0.4		0.45	A-7
実施例 8	AM 91.65	DMA PA 4	AA 4	SMS 0.25	MBA 0.1		0.08	A-8
実施例 9	AM 93.33	DM 4	IA 2	SMS 0.57	MBA 0.1		0.10	A-9
比較例 5	AM 93.9	DM 4	IA 2		MBA 0.1		0.45	C-5
比較例 6	AM 93.9	DM 4	IA 2		MBA 0.1		0.08	C-6
比較例 7	AM 93.9	DM 4	IA 2		MBA 0.1	レフタス系		C-7
比較例 8	AM 93.6	DM 4	IA 2		MBA 0.4		0.45	C-8
比較例 9	AM 93.6	DM 4	IA 2		MBA 0.4		0.45 2)	C-9
比較例 10	AM 91.65	DMA PA 4	AA 4	VS 0.25	MBA 0.1		0.08 3)	C-10

AM: アクリルアミド、 DM: N, N-ジメチルアミノエチルメタアクリレート、 IA: イタコン酸、  
 SMS: メタリルスルホン酸ナトリウム、 MBA: メチレンビスアクリルアミド、  
 DMA PA: N, N-ジメチルアミノプロピルアクリルアミド、 AA: アクリル酸、  
 VS: ビニルスルホン酸ナトリウム

1) 4, 4'-アゾビス-4-シアノ吉草酸

2) アリルアルコール使用 3) イソプロピルアルコール使用

[0119]

[Table 4]

	15% 製品 (cps /25℃)	10% 製品 (cps /25℃)	重量平均 分子量 (a) (万)	重量平均 慣性半径 (b) (nm)	(b) —— (a)	数平均 分子量 (c) (万)	(a) —— (c)	分子量 100 万 以上 (%)	水和径 (nm)
A-6	5000	960	359	94.6	0.0000264	131	2.74	74.5	140
A-7	3000	620	407	93.1	0.0000229	104	3.91	65.2	200
A-8	11000	1980	340	90.6	0.0000266	123	2.76	73.0	150
A-9	1500	340	292	75.0	0.0000257	101	2.89	65.7	140
C-5	9200	1630	84.5	38.8	0.0000459	36.9	2.29	27.8	86
C-6	ゲル化								
C-7	8700	1700	91.0	49.9	0.0000548	39.0	2.33	26.9	156
C-8	ゲル化								
C-9	10000	1860	121	57.1	0.0000472	41.0	2.95	33.1	65
C-10	6800	1170	90	43.0	0.0000478	35.0	2.57	26.4	78

C-5~C-10の水和径は、コールターN4の散乱強度(カウンタ数)が5000以下であり、本来測定できないが、散乱強度5000以下における参考値を示す。

Next, the application at the time of using the polymer obtained in the example and the example of a comparison as an internal form force enhancement agent is shown.

1% slurry of L-BKP of the degree of beating (Canadian standard freeness) CSF 400 obtained from the application 1 corrugated-paper waste paper -- a sulfuric-acid band -- 0.5% for pulp -- it added and stirred for 3 minutes. pH of the pulp slurry at this time was 6.0. then -- while stirring -- 1% water solution of a polymer A-6 -- nonvolatile matter criteria -- 0.5% for pulp -- it added and stirring was further continued for 3 minutes. After an appropriate time, measurement of freeness (JIS-P8112) and paper making with a TAPPI square shape sheet machine were performed using the obtained pulp slurry. 110 degrees C dries for 3 minutes with a drum dryer, and the wet sheet which carried out paper making is basis-weight 100 g/m<sup>2</sup>. The handmade paper was obtained. the ratio after carrying out gas conditioning of the obtained \*\*\*\* in 20 degrees C and RH65% of air conditioned room for 24 hours or more -- bursting strength (JIS-P8112) and Z-axis reinforcement (JAPAN TAPPI00000) were measured. A polymer A-7 to A-9 and a polymer C-5, C-7, C-9, and actuation with the same said of C-10 were performed. The result was shown in Table 5 [Table 5].

[0120]

[Table 5]

	ポリマー	ろ水度 (ml)	比破裂強度	Z軸強度 (kg・cm)
	無添加	420	3.30	3.15
実 施 例	A-6	460	4.44	5.90
	A-7	480	4.50	6.00
	A-8	455	4.40	5.91
	A-9	450	4.35	5.88
比 較 例	C-5	430	3.90	4.20
	C-7	445	3.88	4.50
	C-9	440	3.87	4.44
	C-10	440	3.94	4.30

[0121]

[Effect of the invention -1] The acrylamide system polymer by this invention of having physical properties as shown in Tables 2 and 4, and structure is clear. Moreover, although a part of conventional technique was mentioned as the example of a comparison, neither of the polymerizations can obtain the polymer which has such new structure and a physical-properties value.

[0122] Furthermore, as a result, as shown in the application (Table 5), there is also no paper durability on-the-strength manifestation effectiveness in the former, and it turns out that the acrylamide system polymer by this invention is high.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 10 aforementioned reaction container for 306g of pure water.

[0123] 60g of water solutions which, on the other hand, dissolved 0.24g of 4 and 4'-azobis-4-cyano valeric acids of the solution which carried out the mixed dissolution of 283g [ of acrylamide water solutions ] and methylenebis acrylamide 0.31g and the 1.58g of the sodium methallylsulfonate 50%, and 84% of pure parts was adjusted, it applied for 150 minutes into the reaction container, respectively, and equal dropping was carried out. In the meantime, the temperature in a reaction container was kept at 80 degrees C. The acrylamide system polymer water solution with a Brookfield viscosity [ in 25 degrees C ] of 12000cps was obtained after dropping termination by continuing a polymerization for 3 hours, cooling at 80 degrees C, and terminating a reaction. This polymer is set to A-10. It was 23.8% when asked for bone-dry polymer concentration by weighing 1g precisely in the aluminum cup of weight known of A-10, and drying it with 105-degree C hot air drying equipment after dilution with about 1g pure water for 3 hours. Moreover, it was 1,760,000 when the weight average molecular weight of A-10 was measured by the above-mentioned approach.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 11 aforementioned reaction container for 288g of pure water.

[0124] On the other hand, the mixed dissolution of the 0.24g of the 4 and 4'-azobis-4-cyano valeric acids of 283g [ of 50% acrylamide water solutions ] and methylenebis acrylamide 0.31g, 1.58g of sodium methallylsulfonate, and 84% of pure parts was carried out, and a monomer and initiator mixed liquor were adjusted.

[0125] Then, equal dropping was carried out, having initiator applied [ this monomer and ] them for 150 minutes into the reaction container. In the meantime, the temperature in a reaction container was kept at 80 degrees C. Moreover, it was careful of the temperature of a monomer and initiator mixed liquor for a monomer not to deposit so that it might keep at 15-25 degrees C and a polymerization might not arise before dropping. The monomer before dropping and the existence of polymerization generating of initiator mixed liquor left the mixed liquor of these conditions for 2 hours, and it was checked from adding in a methanol.

[0126] The acrylamide system polymer water solution with a Brookfield viscosity [ in 25 degrees C ] of 3340cps was obtained after dropping termination by continuing a polymerization for 3 hours, cooling at 80 degrees C, and terminating a reaction. This polymer is set to A-11. Many physical-properties values of A-11 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 12 aforementioned reaction container for 293g of purity.

[0127] On the other hand, they are 2823g [ of 50% acrylamide water solutions ], and methylenebis acrylamide 0.31g, sodium methallylsulfonate 3.18g and 2, and 2'-azobis-2-methyl-N. -(2-hydroxyethyl)- The water solution which carried out the mixed dissolution of the propione amide 0.25g was adjusted, it applied for 150 minutes into the reaction container, and equal dropping was carried out. In the meantime, the temperature of a monomer and an initiator mixed solution kept the temperature in a reaction container at 80 degrees C during dropping again at 15-25 degrees C.

[0128] The acrylamide system polymer water solution with a Brookfield viscosity [ in 25 degrees C ] of 3770cps was obtained after dropping termination by continuing a polymerization for 3 hours, cooling at 80 degrees C, and terminating a reaction. This polymer is set to A-12. Many physical-properties values of A-12 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 13 aforementioned reaction container for 296g of pure water.

[0129] On the other hand, the water solution which carried out the mixed dissolution of the 0.36g of the 4 and 4'-azobis-4-cyano valeric acids of 421g [ of 50% acrylamide water solutions ] and methylenebis acrylamide 0.46g, 6.22g of sodium methallylsulfonate, and 84% of pure parts was adjusted, it applied for 150 minutes into the reaction container, and equal dropping was carried out. In the meantime, the temperature of a monomer and initiator mixed liquor kept constant 80 degrees C of temperature in a reaction container at 15-25 degrees C during dropping.

[0130] The acrylamide system polymer water solution with a Brookfield viscosity [ in 25 degrees C ] of 20000cps was obtained after dropping termination by continuing a polymerization for 3 hours, cooling at 80 degrees C, and terminating a reaction. This polymer is set to A-13. Many physical-properties values of A-13 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 14 aforementioned reaction container for 325g of pure water.

[0131] On the other hand, the mixed dissolution of the 0.93g of the 4 and 4'-azobis-4-cyano valeric acids of 550g [ of 50% acrylamide water solutions ] and methylenebis acrylamide 14.4g, 111g of sodium methallylsulfonate, and 84% of pure parts was carried out, and a monomer and initiator mixed liquor were adjusted.

[0132] Then, equal dropping was carried out, having monomer initiator applied [ this ] it for 150 minutes into the reaction container. In the meantime, the temperature in a reaction container was kept at 80 degrees C. Moreover, the temperature of monomer initiator mixed liquor was kept at 15-25 degrees C.

[0133] The acrylamide system polymer water solution with a Brookfield viscosity [ in 25 degrees C ] of 1070cps was obtained after dropping termination by continuing a polymerization for 3 hours, cooling at 80 degrees C, and terminating a reaction. This polymer is set to A-14. Many physical-properties values of A-14 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 15 aforementioned reaction container for 203g of pure water.

[0134] On the other hand, the mixed dissolution of the 0.66g of the 4 and 4'-azobis-4-cyano valeric acids of 747g [ of 60% acrylamide water solutions ] and methylenebis acrylamide 1.02g, 52.8g of sodium methallylsulfonate, and 84% of pure parts was carried out, and the monomer and the initiator mixed solution were adjusted.

[0135] Then, equal dropping was carried out, having initiator covered [ this monomer and ] them for 150 minutes into the reaction container. In the meantime, the temperature of a monomer and an initiator mixed solution kept the temperature in a reaction container at 80 degrees C again at 15-25 degrees C.

[0136] The acrylamide system polymer water solution with a Brookfield viscosity [ in 25 degrees

C ] of 47600cps was obtained after dropping termination by continuing a polymerization for 3 hours, cooling at 80 degrees C, and terminating a reaction. This polymer is set to A-15. Many physical-properties values of A-15 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example of comparison 11 aforementioned reaction container for 363g of pure water.

[0137] On the other hand, equal dropping was carried out, having poured [ which carried out the mixed dissolution of the 0.24g of the 4 and 4'-azobis-4-cyano valeric acid of 284g / of 50% acrylamide water solutions /, and methylenebis acrylamide 0.31g, and 84% of pure parts ] it for 150 minutes into the reaction container. In the meantime, the mixed solution kept constant 80 degrees C of temperature in a reaction container at 15-25 degrees C or less during dropping. However, in the middle of dropping, reaction mixture became hyperviscosity, and the fluidity of it was lost, and, finally it was gelled. This gelation object is set to C-11. Even if it diluted C-11 with water more than it, the distributed dissolution of it was not able to be carried out, and it was not able to acquire many physical-properties values.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example of comparison 12 aforementioned reaction container for 228g of pure water.

[0138] Equal dropping was carried out having poured [ which, on the other hand, dissolved 0.24g of the 4 and 4'-azobis-4-cyano valeric acid of the solution which mixed 283g / of acrylamide water solutions /, and methylenebis acrylamide 0.31g and isopropyl alcohol 30g 50%, and 84% of pure parts / 60g ] it for 150 minutes into the reaction container, respectively. In the meantime, the temperature in a reaction container was kept at 80 degrees C.

[0139] The acrylamide system polymer water solution with a Brookfield viscosity [ in 25 degrees C ] of 13300cps was obtained after dropping termination by continuing a polymerization for 3 hours, cooling at 80 degrees C, and terminating a reaction. This polymer is set to C-12. Many physical-properties values of C-12 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example of comparison 13 aforementioned reaction container for 217g of pure water.

[0140] On the other hand, equal dropping was carried out, having poured [ which carried out the mixed dissolution of the 1.96g of the 4 and 4'-azobis-4-cyano valeric acids of 766g / of 50% acrylamide water solutions /, and methylenebis acrylamide 17.0g, and 84% of pure parts ] it for 150 minutes into the reaction container. In the meantime, the temperature of a monomer and an initiator mixed solution kept the temperature in a reaction container at 80 degrees C at 15-25 degrees C. However, it was in the middle of dropping, and reaction mixture became hyperviscosity, and the fluidity of it was lost, and it was gelled. This gelation object is set to C-13. Even if it diluted C-13 with water more than it, the distributed dissolution of it was not able to be carried out, and it was not able to acquire many physical-properties values.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example of comparison 14 aforementioned reaction container for 167g of pure water.

[0141] On the other hand, equal dropping was carried out, having covered [ which carried out the mixed dissolution of the 0.84g of the 4 and 4'-azobis-4-cyano valeric acids of 8312g / of 60% acrylamide water solutions /, and methylenebis acrylamide 1.1g, and 84% of pure parts ] it for 150 minutes. In the meantime, the temperature of a monomer and an initiator mixed solution kept the temperature in a reaction container at 80 degrees C again at 15-25 degrees C. However, it was in the middle of dropping, and reaction mixture became hyperviscosity, and the fluidity of it was lost, and it was gelled. This gelation polymer is set to C-14. Even if it diluted C-14 with water more than it, the distributed dissolution of it was not able to be carried out, and it was not able to acquire many physical-properties values.

[0142] Many physical-properties values of the polymer C-11 obtained in the polymer A-10 to A-15 and the examples 11-14 of a comparison which were acquired in the examples 10-15 - C14 were collectively shown in Table 6 and 7.

[0143]

[Table 6]

	実施例						比較例			
	10	11	12	13	14	15	11	12	13	14
AM (wt%)	99.4	99.4	98.9	98.6	83	94.9	99.9	99.9	98.0	99.9
MBA (wt%)	0.1	0.1	0.1	0.1	2.0	0.1	0.1	0.1	2.0	0.1
SMS (wt%)	0.5	0.5	1.0	1.3	15.0	5.0	0	0	0	0
開始剤 <sup>1)</sup> (g/モル)	A 0.1	A 0.1	B 0.12	A 0.1	A 0.2	A 0.1	A 0.1	A 0.1	A 0.3	A 0.1
DPC <sup>2)</sup> (%)	23.8	27.4	27.4	31.9	43.1	53.9	—	25.6	—	—
粘度 (ps)	120	33.4	37.7	200	10.7	476	ゲル	133	ゲル	ゲル
M <sub>w</sub> <sup>3)</sup> (万)	176	90.5	130	312	77.3	62	—	36.6	—	—

1) 開始剤 A : 4, 4'-アゾビス-4-シアノ吉草酸  
 B : 2, 2'-アゾビス-2-メチル-N-(2-ヒドロキシエチル)-プロピオンアミド

2) DPC : 絶乾ポリマー濃度

3) M<sub>w</sub> : 重量平均分子量

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 16 aforementioned reaction container for 355g of pure water.

[0144] On the other hand, the mixed dissolution of 263g [ of 50% acrylamide water solutions ] and methylenebis acrylamide 0.25g, 1.49g [ of sodium methallylsulfonate ], N, and N-dimethylaminoethyl METARI rate 15.7g and the itaconic acid 5.2 was carried out, and pH was adjusted to 4.2 by HCl 35%.

[0145] Moreover, 60g of water solutions which dissolved 0.24g of 4 and 4'-azobis-4-cyano valeric acids of 84% of pure parts was adjusted.

[0146] Next, equal dropping was carried out, having poured [ above-mentioned / both ] it for 150 minutes into the reaction container, respectively. In the meantime, the temperature in a reaction container was kept at 80 degrees C.

[0147] The acrylamide system polymer water solution with a Brookfield viscosity [ in 25 degrees C ] of 8950cps was obtained after dropping termination by continuing a polymerization for 3 hours, cooling and terminating a reaction at 80 degrees C. This polymer is set to A-16. Many physical-properties values of A-16 were measured like the example 10.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 17 aforementioned reaction container for 286g of pure water.

[0148] On the other hand, the mixed dissolution of 394g [ of 50% acrylamide water solutions ] and methylenebis acrylamide 0.46g, 6.30g of sodium methallylsulfonate, 18.8g of N,N-dimethylaminopropyl acrylamide, 5.94g of itaconic acids, and the 5.48g of the acrylic acids was carried out, and pH was adjusted to 4.2 by HCl 35%.

[0149] Moreover, 60g of water solutions which dissolved 0.36g of 4 and 4'-azobis-4-cyano valeric acids of 84% of pure parts was adjusted.

[0150] Next, equal dropping was carried out, having poured [ above-mentioned / both ] it for 150 minutes into the reaction container, respectively. In the meantime, the temperature in a reaction container was kept at 80 degrees C.

[0151] The acrylamide system polymer water solution with a Brookfield viscosity [ in 25 degrees C ] of 12000cps was obtained after dropping termination by continuing a polymerization for 3 hours, cooling and terminating a reaction at 80 degrees C. This polymer is set to A-17. Many physical-properties values of A-17 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the

example 18 aforementioned reaction container for 173g of pure water.

[0152] On the other hand, the mixed dissolution of 730g [ of acrylamide water solutions ] and methylenebis acrylamide 1.67g, 25.7g of sodium methallylsulfonate, and the 9.75g of the acrylic acids was carried out 50%, and the sulfuric acid adjusted pH to 4.2 40%.

[0153] Moreover, 60g of water solutions which dissolved 1.08g of 2 and 2'-azobis-2-methyl propione amidine hydrochlorides was adjusted.

[0154] Next, equal dropping was carried out, having poured [ above-mentioned / both ] it for 150 minutes into the reaction container, respectively. In the meantime, the temperature in a reaction container was kept at 80 degrees C.

[0155] The acrylamide system polymer water solution with a Brookfield viscosity [ in 25 degrees C ] of 25500cps was obtained after dropping termination by continuing a polymerization for 3 hours, cooling and terminating a reaction at 80 degrees C. This polymer is set to A-18. Many physical-properties values of A-18 were measured like the example 1.

Using 3 opening flask equipped with the agitator, the reflux cooling pipe, and the thermometer as an example of comparison 15 reaction container, the mixed dissolution of 409g [ of pure water ], 263g [ of 50% acrylamide water solutions ], and methylenebis acrylamide 0.19g, N, and N-dimethylaminoethyl METARI rate 15.7g and the 5.21g of the itaconic acids was carried out, and the temperature up of the pH was carried out to 35 degrees C after adjusting to 4.2 by HCl 35%. There, when 1.0g of 2 and 2'-azobis-2-(2-imidazoline-2-IRU) propane hydrochlorides was added there, initiation of a polymerization was checked after the 20 minutes, and whenever [ reaction container internal temperature ] amounted to 93 degrees C after the 20 minutes further. After continuing a polymerization then for 2 hours, the acrylamide system polymer water solution with a Brookfield viscosity [ in 25 degrees C ] of 46100cps was obtained by cooling and terminating a reaction. This polymer is set to C-15. Many physical-properties values of C-15 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into an example of comparison 16 reaction container (said 5 opening flask) for 278g of pure water.

[0156] On the other hand, the mixed dissolution of 397g [ of 50% acrylamide water solutions ] and methylenebis acrylamide 0.31g, N, and N-dimethylaminoethyl METARI rate 23.5g and the 7.8g of the itaconic acids was carried out, and pH was adjusted to 4.2 by HCl 35%.

[0157] Moreover, 60g of water solutions which dissolved 1.07g of 4 and 4'-azobis-4-cyano valeric acids of 84% of pure parts was adjusted.

[0158] Next, although equal dropping of both the above-mentioned water solutions was carried out like the example 10 into the reaction container, respectively, it was in the middle of dropping, and the fluidity of reaction mixture was lost and it gelled. This gelation polymer is set to C-16. Even if it diluted C-16 more than it, the distributed dissolution of it was not able to be carried out, and it was not able to measure many physical-properties values.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into an example of comparison 17 reaction container (said 5 opening flask) for 330g of pure water.

[0159] On the other hand, the mixed dissolution of the allyl alcohol 23.7g was carried out as 397g [ of 50% acrylamide water solutions ], N, and N-dimethylaminoethyl METARI rate 21.4g, 8.85g of itaconic acids, and a regulator, and pH was adjusted to 4.2 by HCl 35%.

[0160] Moreover, 60g of water solutions which dissolved 0.9g of 4 and 4'-azobis-4-cyano valeric acids of 84% of pure parts was adjusted.

[0161] Next, equal dropping was carried out, having poured [ above-mentioned / both ] it for 150 minutes into the reaction container, respectively. In the meantime, the temperature in a reaction container was kept at 80 degrees C. The acrylamide system polymer water solution with a Brookfield viscosity [ in 25 degrees C ] of 3890cps was obtained after dropping termination by continuing a polymerization for 3 hours, cooling at 80 degrees C, and terminating a reaction. This polymer is set to C-17. Many physical-properties values of C-17 were measured like the example 1.

[0162] Many physical-properties values of the polymer C-15 obtained in the polymer A-16 to A-18 and the examples 15-17 of a comparison which were acquired in the examples 16-18 - C17 were collectively shown in Table 7.



[0163]

[Table 7]

	実 施 例			比 較 例		
	1 6	1 7	1 8	1 5	1 6	1 7
AM (モル%)	92.5	91.1	94.8	92.4	92.9	94.0
MBA (モル%)	0.08	0.1	0.2	0.06	0.1	0
SMS (モル%)	0.47	1.33	3.0	0	0	0
DM <sup>1)</sup> (モル%)	5	4	—	5	5	4
ITA <sup>2)</sup> (モル%)	2	1.5	—	2	2	2
AA <sup>3)</sup> (モル%)	0	2	2	0	0	0
開始剤 <sup>4)</sup> (g/モル)	A 0.1	A 0.1	C 0.2	D 0.5	A 0.3	A 0.22
DPC (%)	22.1	33.2	43.9	23.9	—	31.1
粘度 (ps)	89.5	120	255	461	GEL	38.9
Mw (万)	320	264	184	41.0	—	16.0

1) DM: ジメチルアミノエチルメタクリレート

2) ITA: イタコン酸

3) AA: アクリル酸

4) 開始剤 C: 2, 2'-アゾビス-2-メチルプロピオンアミジン塩酸塩  
D: 2, 2'-アゾビス-2-(2-イミダゾリン-2-イル)

Next, the application at the time of using the polymer obtained in the example and the example of a comparison as an internal form force enhancement agent is shown.

the L-BKP1% slurry of an application 2-3CSF400 -- a sulfuric-acid band -- 0.5% for pulp -- it added and stirred for 3 minutes. pH of the pulp slurry at this time was 6.0. then -- while stirring -- 1% water solution of a polymer A-16 -- nonvolatile matter criteria -- 0.5% for pulp -- it added and stirring was further continued for 3 minutes. After an appropriate time, measurement of freshness (JIS-P8112) and paper making with a TAPPI square shape sheet machine were performed using the obtained pulp slurry. 110 degrees C dries for 3 minutes with a drum dryer, and the wet sheet which carried out paper making is basis-weight 100 g/m<sup>2</sup>. The handmade paper was obtained. the ratio after carrying out gas conditioning of the obtained \*\*\*\* in 20 degrees C and RH65% of air conditioned room for 24 hours or more -- bursting strength (JIS-P8112) and Z-axis reinforcement (internal bond-tester and Kumagaya Riki Kogyo K.K. make) were measured. A polymer A-17 and a polymer C-15, and actuation with the same said of C-17 were performed. The result was shown in Table 8.

[0164]

[Table 8]

	添加樹脂	比破裂強度 (Kg/cm <sup>2</sup> )	濾水度 (ml)	Z軸強度 (Kg-cm)
	無添加	3.31	415	3.12
応用例 2	A-7	4.21	465	5.83
応用例 3	A-8	4.33	460	5.76
比較応用例 1	C-5	3.89	430	4.14
比較応用例 2	C-7	3.99	440	4.23

[0165]

[Effect of the invention -2] Though it is the high concentration which is not seen by the former and the amount of macromolecules as shown after the example 10, the acrylamide system polymer water solution by this invention is the aqueous polymerization object of hypoviscosity, although it is high concentration therefore, becomes reducible [ the freight per solid content ], and is economically excellent. Furthermore, when this polymer is used as a paper reinforcing agent, the thing which bring about the conventional paper reinforcing agent and the engine performance more than equivalent and to excel is clear.

Acrylamide 330g, 1g [ of sodium methallylsulfonate ], and methylenebis acrylamide 0.5g and 558g of city waters are added to the 1l. 4-inlet separable flask equipped with example 19 stirrer, a thermometer, a reflux condenser, and nitrogen installation tubing 40%, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 7400cps in 25 degrees C and pH4.2 was obtained. The absolute molecular weight determined by said measuring method was 2,400,000. This product is set to A.

Acrylamide 330g, dimethylaminoethyl methacrylate 14g, 1g [ of sodium methallylsulfonate ], and methylenebis acrylamide 0.5g and 615g of city waters are added to the example 20 aforementioned separable flask 40%, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 7000cps in 25 degrees C and pH4.2 was obtained. The absolute molecular weight determined by said measuring method was 2,500,000. This product is set to B.

40% acrylamide 330g, dimethylaminoethyl methacrylate 16g, 8g [ of 80% acrylic acids ], 3g [ of itaconic acids ], 1g [ of sodium methallylsulfonate ], and methylenebis acrylamide 0.5g and 669g of city waters are added to the example 21 aforementioned separable flask, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 5900cps in 25 degrees C and pH4.2 was obtained. The absolute molecular weight determined by said measuring method was 2,800,000. This product is set to C.

40% acrylamide 330g, dimethylaminoethyl methacrylate 5g, 80%N-METAKURIROIKISHI ethyl trimethylammonium chloride 18g, 10g [ of 80% acrylic acids ], 1g [ of sodium methallylsulfonate ], and methylenebis acrylamide 0.5g and 698g of city waters are added to the example 22 aforementioned separable flask, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 6200cps in 25 degrees C and pH4.2 was obtained. The absolute molecular

weight determined by said measuring method was 2,700,000. This product is set to D.

40% acrylamide 330g, 80%N-methacryloyloxy-ethyl trimethylammonium chloride 25g, 10g [ of 80% acrylic acids ], 1g [ of sodium methallylsulfonate ], and methylenebis acrylamide 0.5g and 710g of city waters are added to the example 23 aforementioned separable flask, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 6800cps in 25 degrees C and pH4.2 was obtained. The absolute molecular weight determined by said measuring method was 2,600,000. This product is set to E.

Acrylamide 330g, 20g [ of 80% acrylic acids ], 1g [ of sodium methallylsulfonate ], and methylenebis acrylamide 0.5g and 645g of city waters are added to the example 24 aforementioned separable flask 40%, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 5400cps in 25 degrees C and pH4.2 was obtained. The absolute molecular weight determined by said measuring method was 2,500,000. This product is set to F.

40% acrylamide 330g, 12g [ of 80% acrylic acids ], 5g [ of itaconic acids ], 1g [ of sodium methallylsulfonate ], and methylenebis acrylamide 0.5g and 615g of city waters are added to the example 25 aforementioned separable flask, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 61000cps in 25 degrees C and pH4.2 was obtained. The absolute molecular weight determined by said measuring method was 2,400,000. This product is set to G.

Acrylamide 330g, 1g of sodium methallylsulfonate, and 555g of city waters are added to the example of comparison 18 aforementioned separable flask 40%, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 8300cps in 25 degrees C and pH4.2 was obtained. The absolute molecular weight determined by said measuring method was 700,000. This product is set to H.

Acrylamide 330g, methylenebis acrylamide 0.5g, and 553g of city waters are added to the example of comparison 19 aforementioned separable flask 40%, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 5400cps in 25 degrees C and pH4.2 was obtained. The absolute molecular weight determined by said measuring method was 900,000. This product is set to I.

Acrylamide 330g, dimethylaminoethyl methacrylate 14g, 1g of sodium methallylsulfonate, and 607g of city waters are added to the example of comparison 20 aforementioned separable flask 40%, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 8000cps in 25 degrees C and pH4.2 was obtained. The absolute molecular weight determined by said measuring method was 970,000. This product is set to J.

Acrylamide 330g, dimethylaminoethyl methacrylate 16g, 8g of 80% acrylic acids, 3g of itaconic acids, 1g of sodium methallylsulfonate, and 659g of city waters are added to the example of comparison 21 aforementioned separable flask 40%, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and

carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 6700cps in 25 degrees C and pH4.2 was obtained. The absolute molecular weight determined by said measuring method was 810,000. This product is set to K. 40% acrylamide 330g, dimethylaminoethyl methacrylate 5g, 80%N-methacryloyloxy-ethyl trimethylammonium chloride 18g, 10g of 80% acrylic acids, 1g of sodium methallylsulfonate, and 683g of city waters are added to the example of comparison 22 aforementioned separable flask, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 6000cps in 25 degrees C and pH4.2 was obtained. The absolute molecular weight determined by said measuring method was 1,000,000. This product is set to L.

40% acrylamide 330g, 80%N-methacryloyloxy-ethyl trimethylammonium chloride 25g, 10g of 80% acrylic acids, 1g of sodium methallylsulfonate, and 707g of city waters are added to the example of comparison 23 aforementioned separable flask, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 7100cps in 25 degrees C and pH4.2 was obtained. The absolute molecular weight determined by said measuring method was 1,100,000. This product is set to M. Acrylamide 330g, 20g of 80% acrylic acids, 1g of sodium methallylsulfonate, and 642g of city waters are added to the example of comparison 24 aforementioned separable flask 40%, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 6900cps in 25 degrees C and pH4.2 was obtained. The absolute molecular weight determined by said measuring method was 890,000. This product is set to N.

Acrylamide 330g, 12g of 80% acrylic acids, 5g of itaconic acids, 1g of sodium methallylsulfonate, and 638g of city waters are added to the example 26 aforementioned separable flask 40%, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 73000cps in 25 degrees C and pH4.2 was obtained. The absolute molecular weight determined by said measuring method was 880,000. This product is set to O.

[0166] the pulp slurry of 1.0% of concentration which is degree-of-beating CSF(Canadian standard freeness) 420ml obtained from applications 4-10 and the comparison application 3 - 10 corrugated-paper waste paper -- an aluminum sulfate -- dry weight criteria -- 1.0% for pulp -- it added and stirred for 1 minute. pH of the pulp slurry at this time was 5.0. moreover, actuation that it is the same except adding a sodium hydroxide just before adding an aluminum sulfate -- adjusting -- pH of a pulp slurry -- 5.0 and 6. -- it was 0 and 7.0. Subsequently, 0.5% for pulp was added for the paper reinforcing agent obtained in the example 19 on desiccation criteria, and stirring was continued for 1 more minute. Paper making was carried out with the TAPPI square shape sheet machine using the obtained pulp slurry. The wet sheet which carried out paper making performs 110 degrees C and desiccation during 3 minutes with a drum dryer, and is basis-weight 150 g/m<sup>2</sup>. The handmade paper was obtained. Let this \*\*\*\* be an application 4. JIS after performing seasoning of 24 hours or more for obtained \*\*\*\* in 20 degrees C and RH65% of air conditioned room -- law -- following -- a ratio -- bursting strength (JIS-P8112) and a ratio -- measurement (JIS-P8121) of compressive strength (JIS-P8126) and freshness was performed. The result was shown in Tables 8-10.

[0167] In the approach of obtaining the converted paper of an application 4, the paper of applications 5-10 and the comparison applications 3-10 was completely obtained in the same

conditions and identity operation except changing the paper reinforcing agent (A) of an example 19. moreover, the ratio of the paper of applications 5-10 and the comparison applications 3-10 - bursting strength and a ratio -- measurement of compressive strength and freshness was also completely performed in the same conditions and identity operation with evaluation of the paper of an application 4.

[0168]

[Table 9]

(抄紙 pH5.0 )

	添加樹脂	比破裂強度 (kgf/cm <sup>2</sup> )	比圧縮強度 (N・m <sup>2</sup> /g)	漉水度 (ml)
	無 添 加	3.52	15.3	420
応用例 4	A	4.72	19.4	445
応用例 5	B	4.81	21.0	465
応用例 6	C	4.85	21.4	465
応用例 7	D	4.86	21.0	470
応用例 8	E	4.80	20.6	480
応用例 9	F	4.87	21.6	480
応用例 10	G	4.90	21.6	475
比較応用例 1	H	4.22	18.1	430
比較応用例 2	I	4.24	18.3	440
比較応用例 3	J	4.38	18.5	440
比較応用例 4	K	4.20	18.2	440
比較応用例 5	L	4.21	18.0	430
比較応用例 6	M	4.25	18.6	420
比較応用例 7	N	4.30	19.0	440
比較応用例 8	O	4.31	19.1	435

[0169]

[Table 10]

(抄紙pH6.0)

	添加樹脂	比破裂強度 (Kgf/cm <sup>2</sup> )	比圧縮強度 (N・m <sup>2</sup> /g)	漉水度 (ml)
	無添加	3.65	16.0	425
応用例 1	A	4.70	19.5	450
応用例 2	B	4.85	21.3	465
応用例 3	C	4.91	21.8	460
応用例 4	D	4.90	21.5	465
応用例 5	E	4.88	21.0	475
応用例 6	F	4.80	20.2	470
応用例 7	G	4.84	21.0	465
比較応用例 1	H	4.25	18.2	420
比較応用例 2	I	4.26	18.3	430
比較応用例 3	J	4.43	19.0	440
比較応用例 4	K	4.25	18.9	430
比較応用例 5	L	4.22	18.5	425
比較応用例 6	M	4.25	19.0	425
比較応用例 7	N	4.26	18.6	450
比較応用例 8	O	4.28	19.4	445

[0170]

[Table 11]

(抄紙pH7.0)

	添加樹脂	比破裂強度 (Kgf/cm <sup>2</sup> )	比圧縮強度 (N・m <sup>2</sup> /g)	漉水度 (ml)
	無添加	3.55	15.1	420
応用例1	A	4.64	19.1	445
応用例2	B	4.81	21.0	455
応用例3	C	4.88	21.3	460
応用例4	D	4.90	21.6	460
応用例5	E	4.82	20.6	460
応用例6	F	4.76	20.0	450
応用例7	G	4.81	20.7	455
比較応用例1	H	3.92	17.2	425
比較応用例2	I	3.99	17.9	430
比較応用例3	J	4.20	18.9	425
比較応用例4	K	4.22	19.4	430
比較応用例5	L	4.15	18.0	430
比較応用例6	M	4.23	18.7	430
比較応用例7	N	3.89	17.6	440
比較応用例8	O	3.98	18.4	435

[0171]

[Effect of the invention -3] the paper reinforcing agent of the former [ paper reinforcing agent / by this invention ] -- comparing -- a ratio -- bursting strength and a ratio -- it is clear from the result of Tables 8-10 that it is the outstanding paper reinforcing agent which has the description of the paper durability effectiveness which was excellent in compressive strength and freshness being shown, and being hard to be influenced of pH fluctuation by the paper-milling system.

[Translation done.]

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TECHNICAL FIELD

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[Industrial Application] This invention relates to a useful acrylamide system polymer and its water solution in paper manufacture industry, the waste-water-treatment field, the engineering-works construction field, etc. Specifically, it is related with the acrylamide system polymer which controlled the branching structure of cross linkage. The acrylamide system polymer of this invention is useful especially as a paper reinforcing agent excellent in the paper durability enhancing effect in a paper manufacture industrial field.

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PRIOR ART

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[Description of the Prior Art] The acrylamide system polymer is used for various applications from before. Specifically, a paper reinforcing agent, a filtration improvement agent, the yield improver, the flocculant, the object for the secondary productions of petroleum, the dispersant, etc. are known. For those applications, the acrylamide system polymer from about 100,000 to 20 million or more things with various weight average molecular weight is properly used by the purpose, and the polymer which has the straight chain-like molecular structure has mainly been used.

[0003] Molecular weight is made to increase, a paper reinforcing agent etc. giving the partial structure of cross linkage and branching structure, and controlling a viscosity rise of those solutions by using a cross linking agent for an acrylamide system polymer etc., in a paper manufacture industrial field, in recent years, and the attempt which aims at improvement in the engine performance is made.

[0004] For example, the technique which uses the vinyl monomer which has two or more double bonds is in a molecule as a cross linking agent. As a concrete vinyl monomer, 3 functionality monomers, such as divinyl monomers, such as methylenebis acrylamide, methylenebis meta-acrylamide, ethylene glycol diacrylate, and ethylene glycol dimethacrylate, 1 and 3, 5-thoria chestnut roil hexahydro-S-triazine, and triallyl isocyanurate, etc. are known. About the macromolecule quantification technique by the crosslinking reaction only depending on these vinyl monomer, the heterogeneity of the branching structure of cross linkage is large, and the phenomenon of the gelation effectiveness amplifying about polyfunctional monomer is seen, and it can be said that it is still inadequate as a paper reinforcing agent.

[0005] Furthermore, in addition to these cross linking agents, the attempt which manufactures the acrylamide system polymer which has the branching structure of cross linkage is also made by using a specific compound together. For example, combination with the monomer which has a cross linking agent, the 1st class amine, or a hydroxyl group or combination, a cross linking agent and a specific hydrophobic monomer, and the combination which it is with a cross linking agent and an itaconic-acid derivative further are known. However, although macromolecule quantification is attained by hypoviscosity, the result is also fully as a paper reinforcing agent insufficient [ seen from the structure side of a polymer ] also in any, still.

[0006] Moreover, the attempt which manufactures the acrylamide system polymer which has the branching structure of cross linkage also with means other than the branching bridge formation approach by copolymerization using the aforementioned polyfunctional vinyl system monomer is made. The additive for paper manufacture using a reaction with a specific N-permutation acrylamide derivative like N,N-dimethylacrylamide as the example, a persulfuric acid system, or a peroxide system catalyst is proposed. However, although macromolecule quantification is enabled by hypoviscosity about this approach, since the cutting reaction of a polymer chain is also produced, the obtained polymer cannot fully say the effectiveness as a paper reinforcing agent as sufficient thing seen from that structure side, either.

[0007] Moreover, the acrylamide system polymer manufactured in these conventional techniques is usually used for the above-mentioned application as a water solution, it is possible to make it the water solution of concentration 15%, and the manufacture approach of a thing that molecular

weight is about 3 million is proposed. However, \*\* et al. and a high-concentration thing are not known at all, but the concentration is at most 15% - 21%. The reason is that macromolecule quantification which is expected is not made or viscosity becomes very high by the straight chain-like polymer by the concentration beyond this. Moreover, it is because it will become unusable as a paper reinforcing agent -- crosslinking reaction advances unusually, the whole gels and it being high concentration and an interval are not partially obtained in the state of a water solution, or insoluble gel is formed in water -- if it is going to introduce the branching structure of cross linkage into a polymer.

[0008] Although the surface paper durability agent which becomes JP,3-279491,A from the polyacrylamide system polymer water solution of 500 to 5000 cps viscosity and 10 - 30% of concentration is indicated and the range of molecular weight 100,000-3 million is indicated in it, in this approach, there is no concrete description which can attain with a molecular weight of 500,000 or more macromolecule quantification absolutely above 22% concentration.

[0009] Although the improvement in polymer concentration had a merit in respect of the transportation cost, the amount acrylamide system polymer water solution of macromolecules of 22% or more of concentration was not known at all for the above reasons until now.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The purpose of this invention offers the acrylamide system polymer water solution which has the new physical properties which are not known, the acrylamide system polymer water solution which is hypoviscosity comparatively in high concentration in spite of being specifically the amount of macromolecules, and its manufacture approach with the conventional technique.

[0011] Other purposes of this invention are offering the acrylamide system polymer which has the new structure which is not known for the above conventional techniques.

[0012] Furthermore, other purposes of this invention are offering the paper reinforcing agent which consists of this acrylamide system polymer.

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## MEANS

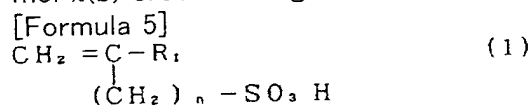
[Means for Solving the Problem] As a result of repeating examination wholeheartedly about the polymerization of an acrylamide system polymer in view of the above-mentioned situation, this invention persons came to acquire the aqueous polymerization object which is hypoviscosity, though it was the high concentration which is not seen by the former and the amount of macromolecules.

[0014] That is, weight average molecular weight (a) is 1,500,000-10,000,000, it is 150nm and the weighted mean radius of inertia (b) of this invention is the acrylamide system polymer the weighted mean radius of inertia (b) as an index which shows an average degree of cross linking, and whose 30 - ratio [ of weight average molecular weight (a) ] (b)/(a) are 0.00004 or less.

[0015] In the acrylamide system polymer of above-mentioned this invention, number average molecular weight (c) is 400,000-5,000,000, and it is desirable that weight-average-molecular-weight (a) and ratio [ of (c) ] (a)/(c) is six or less.

[0016] Polymer concentration is the range which is 22 - 60%, the Brookfield viscosity in 25 degrees C is below 50,000cps (centipoise), and this invention offers the acrylamide system polymer water solution whose weight average molecular weight is 500,000-10 million again.

[0017] Furthermore, this invention is [0018] expressed with the (a) (meta) acrylamide 94-99.98 mol % (b) cross-linking monomer 0.01 - one-mol % and (c) following general formula (1).



(The inside R1 of a formula is a hydrogen atom or the low-grade alkyl group of carbon numbers 1-3, and n is the integer of 1-4) The paper reinforcing agent which consists of a water-soluble polymer obtained [ make / into a constituent / 0.01-5 mol % of one sort or 2 sorts or more of vinyl compounds chosen from vinyl compounds and/or those salts ] by carrying out a polymerization is offered.

[0019] You may change to one sort or two sorts or more of vinyl compounds chosen from the vinyl compounds which copolymerizes [ the above-mentioned monomer of tales doses and ] 0.01 - 20-mol % and/or those salts of (a) as occasion demands.

[0020] the case where it is used as a paper reinforcing agent although the acrylamide system polymer in this invention says the copolymer which contains acrylamide and/or meta-acrylamide as the maximum component to all the monomer components that constitute the polymer formed from acrylamide and/or meta-acrylamide, or an acrylamide system polymer -- acrylamide and/or meta-acrylamide -- more than 50 mol % -- containing -- desirable -- further -- desirable -- 74-99.97-mol % -- it is 94-99.98-mol % especially preferably.

[0021] The weight average molecular weight (a) as used in the field of this invention can be calculated with static light scattering measurement. A value can be acquired by using the light-scattering detection equipment of whenever [ multiple ], and specifically creating a Zimm plot etc. Or it can obtain by creating a debye plot etc. by the GPC-MALLS method which connected the light-scattering detector to GPC whenever [ multiple ].

[0022] moreover, a weighted mean radius of inertia (b) -- above-mentioned GPC-MALLS -- it is

measured by law.

[0023] Generally in the determination of molecular weight by light scattering measurement Basic type  $Kc/R$  of the following light scattering  $(\theta) = 1 - \frac{1}{MwP(\theta)} + 2A_2 c + \dots$  the reduction on-the-strength  $c$  = sample concentration  $Mw$  = weight average molecular weight of the scattered light (Rayleigh multiplier) in the  $R(\theta)$  = include angle  $\theta$ , although an  $A_2 = 2nd$  virial coefficient  $K$  = optical parameter  $P(\theta)$  = include-angle scattering function is used GPC-MALLS as used in the field of this invention by which weight average molecular weight (a) connected the low include-angle light-scattering detector to GPC -- the value which disregarded like law the 2nd term or subsequent ones which is the 2nd virial coefficient shall be said

[0024] moreover, the weighted mean radius of inertia (b) as used in the field of this invention -- the root average of a weighted mean -- square -- the thing of a radius of inertia (Root Mean Square Radius -- generally shown by  $\langle S^2 \rangle^{1/2}$ ) is said.

[0025] In order to get to know the average degree of cross linking of a polymer, it becomes important to get to know the relation between weight average molecular weight and molecule sizes (radius of inertia etc.). Generally, it is known that what has the larger branching degree of cross linking of a polymer is smaller as for the molecule size of the polymer in the same presentation and the same molecular weight. Therefore, ratio [ of both at the time of specifying the range of the weight average molecular weight (a) in an acrylamide system polymer and a weighted mean radius of inertia (b) ]  $(b)/(a)$  can be used as an index which shows an average degree of cross linking.

[0026] As for the weight average molecular weight (a) of the acrylamide system polymer in this invention, 30 - 150nm and  $(b)/(a)$  of 1,500,000-10,000,000, and a weighted mean radius of inertia (b) is 0.00004 or less. When it takes into consideration that it is desirable that the polymer is equipped with the uniform branching structure of cross linkage, preferably, weight average molecular weight (a) is 2,000,000-8,000,000, a weighted mean radius of inertia (b) is 40-120nm, and  $(b)/(a)$  is 0.000035 or less.

[0027] When it takes into consideration that 400,000-5,000,000 have the desirable number average molecular weight (c) of the acrylamide system polymer in this invention, and it is desirable that it is equipped with the branching structure of cross linkage with a uniform polymer although six or less are desirable as for weight-average-molecular-weight (a) and ratio [ of (c) ]  $(a)/(c)$ , still more preferably, number average molecular weight (c) is 500,000-3,000,000, and  $(a)/(c)$  is four or less. in addition, the above-mentioned number average molecular weight (c) -- absolutely -- the thing of number average molecular weight -- it is -- GPC-MALLS -- it is measurable by law. Ratio [ of weight average molecular weight (a) and number average molecular weight (c) ]  $(a)/(c)$  shows the molecular weight distribution of a polymer.

[0028] In the acrylamide system polymer of this invention, although it has 1,000,000 or more molecular weight, when it takes into consideration that 40 % of the weight or more of a rate is desirable, and it is desirable that the polymer is equipped with the uniform branching structure of cross linkage, it is 50 % of the weight or more more preferably, and is 60 % of the weight or more still more preferably. the molecular weight in this case -- GPC-MALLS -- the absolute molecular weight measured by law -- saying -- GPC-MALLS -- it can know from the distribution curve of the absolute molecular weight by law.

[0029] Values, such as molecular weight of the polymer by the above light scattering measurement and a radius of inertia, can measure N / 15 phosphate buffer solutions containing N / 10 sodium nitrates (pH7) as a solvent (eluate).

[0030] In the acrylamide system polymer of this invention, the diameter of hydration by dynamic light scattering is 50-300nm preferably, and is 70-300nm still more preferably. The diameter of hydration by dynamic light scattering says the hydrodynamic diameter by the Einstein-Stokes formula, uses N / 15 phosphate buffer solutions containing N / 10 sodium nitrates (pH7) as a solvent (eluate), and the value (temperature of 20 degrees C) measured by 90 degrees of diffusion angles by 0.1% of polymer concentration is said. Specifically, it can measure with equipments, such as N4 mold submicron particle analysis apparatus of a coal tar company. Data analysis is based on the SDP analysis which used Program CONTIN with the above-mentioned

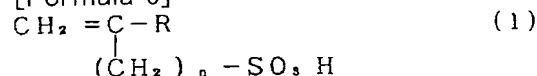
equipment.

[0031] It is 300 to 20,000 centipoise / 25 degrees C that the Brookfield viscosity [ in / in the Brookfield viscosity in 10% water-solution concentration of the acrylamide system polymer of this invention / 20 to 10,000 centipoise / 25 degrees C, or 15% water-solution concentration ] is 100 to 30,000 centipoise / 25 degrees C desirable still more preferably.

[0032] As an example of the acrylamide system polymer of this invention, one sort or the acrylamide system polymer obtained by copolymerizing two or more sorts is mentioned in the compounds shown, for example by acrylamide or meta-acrylamide, and the following general formula (1), or those salts.

[0033]

[Formula 6]



(For the inside R of a formula, a hydrogen atom or a low-grade alkyl group, and n are the integer of 1-8)

In a general formula (1), a low-grade alkyl group is an alkyl group of carbon numbers 1-3 preferably, and are specifically a methyl group, an ethyl group, n-propyl group, and an i-propyl group. The salt is alkali-metal salts, such as sodium and a potassium, ammonium salt, etc. It is expressed with a general formula (1) and an allyl compound sulfonic acid, sodium allylsulfonate, a metallyl sulfonic acid, sodium methallylsulfonate, metallyl sulfonate ammonium, etc. can be illustrated as an example of a sulfonic-acid-ized compound, for example.

[0034] It is 0.05-10-mol % preferably [ it is desirable and ] to 0.01-20-mol % and a pan from it being desirable that the polymer is equipped with the uniform branching structure of cross linkage as an amount of these compounds to the total amount of all the monomers that constitute an acrylamide system polymer although it is 0.005-30-mol %. Moreover, when [ 0.01-5 mol% of ] using it as an internal form force enhancement agent, it is desirable, and 0.05-5-mol % is the most desirable. these compounds -- a kind -- or two or more sorts can be used, using together.

[0035] In addition, the effectiveness as a regulator of acrylamide is indicated by the U.S. Pat. No. 4451628 number about a metallyl sulfonic acid and its salt. However, this approach shows that the acrylamide system polymer of low molecular weight is obtained, and the polymers which controlled branching and the structure of cross linkage of this invention completely differ in the polymer obtained.

[0036] Furthermore, in addition to the compound shown by the general formula (1), the acrylamide system polymer of this invention can be more easily obtained by using a cross-linking monomer.

[0037] When this cross-linking monomer is listed concretely, methylenebis acrylamide, Methylenebis meta-acrylamide, ethylene bis-acrylamide, ethylene bis-meta acrylamide, Ethylene glycol diacrylate, ethylene glycol dimethacrylate, Diethylene glycol diacrylate, diethylene glycol dimethacrylate, Two organic-functions mold cross-linking monomers, such as triethylene glycol diacrylate, triethylene glycol dimethacrylate, a divinylbenzene, and diaryl acrylamide, Or 1, 3, 5-thoria chestnut roil hexahydro-S-triazine, Polyfunctional mold cross-linking monomers, such as triallyl isocyanurate, thoria krill acid pentaerythritol, trimethylol propane acrylate, triacrylformal, and diacryloyl imide, can be illustrated. As an amount of these cross-linking monomers, it is desirable that it is 0.005-5-mol % to the total amount of all the monomers that constitute an acrylamide system polymer. Since it is desirable that the polymer is equipped with the uniform branching structure of cross linkage, it is still more desirable that it is [ 0.01-2 mol ] %, and especially 0.01-1-mol % is desirable. these compounds -- one sort -- or two or more sorts can be used, using together.

[0038] The acrylamide system polymer in this invention can be manufactured also by carrying out copolymerization more than of one sort or it of various vinyl monomers in addition to acrylamide and/or methacrylamide. An ionicity monomer, a hydrophilic monomer, a hydrophobic monomer, etc. are raised to them.

[0039] As an anionic monomer, unsaturated carboxylic acid, such as an acrylic acid, a methacrylic acid, an itaconic acid, a maleic acid, and a fumaric acid, and those salts, a vinyl sulfonic acid, a styrene sulfonic acid, acrylamide methyl propane sulfonic acids, and those salts are mentioned among ionicity monomers, for example.

[0040] As a cationic monomer, amines, those salts (the 4th class ghost is also included), etc., such as N and N-dimethylaminoethyl methacrylate, N, and N-diethylamino ethyl methacrylate, N, and N-dimethylamino ethyl acrylate, N-N-dimethylaminopropyl methacrylamide, and N,N-dimethylaminopropyl acrylamide, can be raised.

[0041] As a hydrophilic monomer, for example Acetone acrylamide, N,N-dimethylacrylamide, N and N-dimethyl methacrylamide, N-ethyl methacrylamide, N-ethyl acrylamide, N, and N-diethyl acrylamide, N-propyl acrylamide, N-acryloyl pyrrolidine, N-acryloyl piperidine, N-acryloyl morpholine, Hydroxyethyl methacrylate, hydroxyethyl acrylate, hydroxypropyl methacrylate, hydroxypropyl acrylate, various kinds of methoxy polyethylene-glycol (meta) acrylate, an N-vinyl-2-pyrrolidone, etc. can be raised.

[0042] As a hydrophobic monomer, for example N and N-G n-propyl acrylamide, N-n-butyl acrylamide, N-n-hexyl acrylamide, N-n-hexyl methacrylamide, N-n-octyl acrylamide, N-n-octyl methacrylamide, N-tert-octyl acrylamide, N-alkyl (meta) acrylamide derivatives, such as N-dodecyl acrylamide and N-n-dodecyl methacrylamide, N and N-diglycidyl acrylamide, N, and N-diglycidyl methacrylamide, N-(4-glycidoxybutyl) acrylamide, N-(4-glycidoxybutyl) methacrylamide, N-(omega-glycidoxy alkyl) (meta) acrylamide derivatives, such as N-(5-glycidoxy pentyl) acrylamide and N-(6-glycidoxy hexyl) acrylamide, Methyl (meta) acrylate, ethyl (meta) acrylate, butyl (meta) acrylate, Lauryl (meta) acrylate, 2-ethylhexyl (meta) acrylate, Acrylate (meta) derivatives, such as glycidyl (meta) acrylate, Olefins, such as acrylonitrile, a methacrylonitrile, vinyl acetate, a vinyl chloride, a vinylidene chloride, ethylene, a propylene, and a butene, styrene, alpha methyl styrene, a butadiene, an isoprene, etc. can be raised.

[0043] The amount of the vinyl monomer used with which copolymerization is presented changes with the classes of vinyl monomer, and those combination, and although there is no \*\*\*\*\* generally, it is in the 0-50-mol range of % in general. the case where an acrylamide system polymer is used as a paper reinforcing agent -- an anionic polymer -- desirable -- 0-20-mol % -- it is more preferably used at 0.5-10-mol % -- having -- and a cationic polymer -- desirable -- 0-20-mol % -- it is more preferably [ 0.5-10 mol% of ] the optimal.

[0044] this invention -- following -- concentration -- the water solution of the acrylamide polymer of 500,000-10,000,000 is offered [ the Brookfield viscosity in 25 degrees C ] for weight average molecular weight by 50,000cps or less in 30-60% of range especially 22 to 60%. The concentration and molecular weight of the range which does not have trouble in a paper reinforcing agent application, for example are 500,000-3 million by 500,000 - 4 million or 50% concentration in 500,000 - 6 million or 40% concentration with 500,000 - 8 million or 30% concentration in general from the desirable homogeneous point of the branching structure of cross linkage at 25% concentration.

[0045] In addition, polymer concentration can be obtained by measuring the bone-dry polymer concentration of a polymer water solution. As a measuring method, a hot-air-drying method, the blanket method, etc. are mentioned.

[0046] As a polymerization method of the acrylamide system polymer in this invention, a radical polymerization is desirable. Although polar solvents, such as water, alcohol, and dimethylformamide, are applicable as a polymerization solvent, when using it as a paper reinforcing agent, it is desirable that it is aqueous polymerization. In the case of aqueous polymerization, it is possible to carry out concomitant use use with organic solvents, such as alcohol, in the range in which a polymer carries out deposit sedimentation and does not spoil dispersibility.

[0047] The batch (batch) polymerization which teaches all monomers to a reaction container by package, and carries out a polymerization is sufficient as the polymerization method of the acrylamide system polymer in this invention. \*\* et al. [ however, ] -- when obtaining 22% or more of high concentration water solution, while especially a part or all of a monomer is dropped into a reaction container, it is more desirable that it is the half-batch (semi batch) polymerization

method which carries out a polymerization. It not only becomes easy to remove the heat of polymerization in monomer high concentration liquid, but by performing a semi batch polymerization method, equalization of the branching structure of cross linkage of a polymer becomes controllable [ becoming easy etc. / the molecular structure ].

[0048] Especially a limit does not have the polymerization concentration shown by the monomer + polymer concentration at the time of a polymerization, and two to 40% of the weight, although it is 5 - 40 % of the weight preferably, in case 22% of the weight or more of a high concentration water solution is obtained, it is usually as follows.

[0049] That is, the polymerization concentration in the case of batch polymerization is 22 - 40 % of the weight in general. Although a polymerization is carried out by concentration lower than 22 % of the weight and the obtained polymerization reaction mixture is not interfered by concentration actuation as a polymer water solution of 22% of the weight or more of concentration, it is disadvantageous in respect of economical efficiency. In the case of semi batch polymerization, the polymerization concentration in the reactor under dropping can be chosen at arbitration by adjusting the initial monomer concentration in a reactor, and the dropping rate of a monomer. However, the polymerization concentration at the time of dropping termination is 22 - 60 % of the weight in general. In this case, there is a disadvantageous point which carried out [ a point ] the polymerization by concentration lower than 22 % of the weight, and was mentioned above by concentration actuation like batch polymerization although it was also possible to have considered as the polymer water solution of 22% of the weight or more of concentration.

[0050] Although there is nothing, if especially a limit of a polymerization initiator is a water-soluble thing, it is desirable. You may add collectively in a monomer water solution, and it may be dropped. As a concrete polymerization initiator, ammonium persulfate, potassium persulfate, sodium persulfate, a hydrogen peroxide, a benzoyl peroxide, tert-butyl peroxide, etc. are mentioned by the persulfate system and the peroxide system, for example. In this case, although it is more desirable to use it independently, it can be used also as a redox system polymerization initiator combining a reducing agent. As a reducing agent, reducing sugars, such as organic amines, such as salts of ionization of a low degree, such as a sulfite, a hydrogensulfite, iron, copper, and cobalt salt, N and N, N', and N'-tetramethyl ethylene diamine, and also an aldose, and a ketose, etc. can be mentioned, for example.

[0051] An azo compound is also the most desirable initiator in this invention. A 2 and 2'-azobis-2-methyl propione amidine hydrochloride, A 2 and 2'-azobis-2,4-dimethylvaleronitrile, 2, and 2'-azobis-N and N'-dimethylene isobutyl amidine hydrochloride, 2 and 2'-azobis-2-methyl-N -(2-hydroxyethyl)- Propione amide, 2, and 2'-azobis -2 -(2-imidazoline-2-IRU)- A propane and its salt, 4, and 4'-azobis-4-cyano valeric acid, its salt, etc. can be used. Furthermore, it is also possible to use together two or more sorts of above-mentioned polymerization initiators. The amount of a polymerization initiator is 0.001 - 5 % of the weight to a monomer in general.

[0052] In the case of a single polymerization initiator, polymerization temperature is 30-90 degrees C in general, and the initiation temperature in the case of a redox system polymerization initiator is 5-50 degrees C in general lower. Moreover, although it is not necessary to maintain at same-during polymerization temperature and you may change suitably with advance of a polymerization, in order to carry out a temperature up by the heat of polymerization generally generated with advance of a polymerization, it may be necessary to add cooling if needed. It is better for inert gas like nitrogen gas to permute with making a polymerization perform promptly, although especially limitation does not have an ambient atmosphere in the polymerization container at that time. Although especially limitation does not have polymerization time amount, it is 1 - 20 hours in general also including the drop time in semi batch polymerization. Although especially limitation does not have Polymerization pH, pH adjustment may be carried out if needed and a polymerization may be performed. In that case, organic acids, such as mineral acids, such as alkalization agents, such as a sodium hydroxide, a potassium hydroxide, and ammonia, a phosphoric acid, a sulfuric acid, and a hydrochloric acid, formic acid, and an acetic acid, etc. are mentioned as an usable pH regulator.

[0053] The acrylamide system polymer which is not known at all conventionally as mentioned



above and its water solution can be obtained, and the polymer and water solution which were obtained can demonstrate many effectiveness which was excellent as a paper reinforcing agent. The case where the acrylamide system polymer of this invention is used for below as a paper reinforcing agent is further explained to a detail.

[0054] It is with what is used for a paper reinforcing agent by adding in a pulp slurry (for internal), and the thing (for outside \*\*) used by applying or sinking into the paper sheet after wire dehydration, and the acrylamide system polymer of this invention can be used for the all.

[0055] The paper reinforcing agent by this invention is usually used by the following approaches. That is, when used as an object for internal, in a pulp slurry, it uses together with fixing agents, such as a sulfuric-acid band, and is added if needed. The amount of the paper reinforcing agent used in this case (solid content) is 0.05 - 3% to pulp solid content in general. moreover, the same as the above by size press, calender spreading, etc., when using it as an object for outside \*\* -- amount use is carried out.

[0056] When using the acrylamide system polymer water solution more than 22% concentration as a paper reinforcing agent, weight average molecular weight should just be 500,000-10 million. Although desirable one has the economically undoubted one where polymer concentration is higher, viscosity is good [ in it being below 20,000cps (centipoise) still more preferably ] at the time of circulation preferably below 50,000cps (centipoise) below 30,000cps (centipoise) from the point of the workability at the time of use.

[0057] In addition, a polymer water solution is used, diluting it suitably.

[0058] By the approach of this invention, the acrylamide system polymer of such new structure nature and its water solution come to be obtained by what kind of reason, or, at present, it is unknown. When the polymer to which the compound shown by general formulas 1 or 2 reacted reacts specifically with the radical in a polymerization and other polymers, or the pendant double bond of a cross-linking monomer reason, branching bridge formation advances efficiently and it is imagined as that from which the acrylamide system polymer which has the much more uniform branching structure of cross linkage is obtained as compared with what is known conventionally as a result. furthermore, since this polymer has the uniform branching structure of cross linkage, it increases the pasting up point between pulp fiber indirectly -- making -- the former -- furthermore, it is thought as an outstanding paper reinforcing agent that various engine performance is demonstrated.

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[Translation done.]

\* NOTICES \*

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- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

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EXAMPLE

[Example] Below, an example explains this invention concretely. In addition, this invention is not limited to these examples. Moreover, especially the thing shown by % below shall mean weight %, unless it refuses.

[0060] The Measuring condition of GPC-MALLS in an example is as follows.

[0061] GPC body: The Showa Denko K.K. make, system 11 column:SHODEX SB 80M eluate: N / 15 phosphate buffer solutions containing N / 10 sodium nitrates (pH7)

rate-of-flow: -- a part for 1.0ml/-- detector: -- the internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into light-scattering detector DAWN example 1 stirrer, a reflux cooling pipe, a thermometer, nitrogen gas installation tubing, and 5 opening flask (it is hereafter called a reaction container) equipped with dropping opening for 500g of pure water whenever [ multiple / of the Wyatt technology company ].

[0062] 60g of water solutions which, on the other hand, dissolved 0.18g of 4 and 4'-azobis-4-cyano valeric acids of the solution which carried out the mixed dissolution of 354.3g [ of acrylamide water solutions ] and methylenebis acrylamide 0.308g and the 0.632g of the sodium methallylsulfonate 40%, and 84% of pure parts was adjusted, it applied for 130 minutes into the reaction container, respectively, and equal dropping was carried out. In the meantime, the temperature in a reaction container was kept at 80 degrees C. The acrylamide system polymer water solution with the nonvolatile matter of 15%, the Brookfield viscosity of 18000cps in 25 degrees C, 10% [ of nonvolatile matters ], and a Brookfield viscosity [ in 25 degrees C ] of 1780cps was obtained after dropping termination by continuing a polymerization for 3 hours, adding water, cooling further, and terminating a reaction at 80 degrees C. This polymer is set to A-1. the weight average molecular weight (a) of A-1, and a weighted mean radius of inertia (b) -- GPC-MALLS -- when measured by law, it was 3050000 or 73.8nm and was (b)/(a) =0.0000242, respectively. Moreover, more absolutely than the law, number average molecular weight (c) was 1250000, and was (a)/(c) =2.44. Furthermore, it was 73.5% when asked for the with a molecular weight of 1 million or more weight rate (d) from the distribution curve. On the other hand, it was 120nm when asked for the diameter of hydration (e) by N4 mold submicron particle analysis apparatus by the coal tar company.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 2 aforementioned reaction container for 560g of pure water.

[0063] On the other hand, the mixed dissolution of the 0.9g of the 4 and 4'-azobis-4-cyano valeric acids of 354.1g [ of 40% acrylamide water solutions ] and methylenebis acrylamide 1.23g, 0.79g of sodium methallylsulfonate, and 84% of pure parts was carried out, and monomer initiator mixed liquor was adjusted.

[0064] Then, equal dropping was carried out, having monomer initiator applied [ this ] it for 150 minutes into the reaction container. In the meantime, the temperature in a reaction container was kept at 80 degrees C. Moreover, the temperature of monomer initiator mixed liquor is kept at 20 degrees C or less, and it was made for a polymerization not to produce it before dropping.

[0065] The acrylamide system polymer water solution with the nonvolatile matter of 15%, the Brookfield viscosity of 2170cps in 25 degrees C, 10% [ of nonvolatile matters ], and a Brookfield viscosity [ in 25 degrees C ] of 330cps was obtained after dropping termination by continuing a

polymerization for 3 hours, adding water, cooling further, and terminating a reaction at 80 degrees C. This polymer is set to A-2. Many physical-properties values of A-2 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 3 aforementioned reaction container for 257.5g of pure water.

[0066] On the other hand, the solution which carried out the mixed dissolution of 532.6g [ of acrylamide water solutions ] and methylenebis acrylamide 0.585g and the 7.865g of the sodium methallylsulfonate 50%, and 60g of water solutions which dissolved NaOH of 0.38g of 4 and 4'-azobis-4-cyano valeric acids of 84% of pure parts, and it and 2 double mol were adjusted further, it applied for 150 minutes into the reaction container, respectively, and equal dropping was carried out. In the meantime, the temperature in a reaction container was kept at 80 degrees C.

[0067] The acrylamide system polymer water solution with the nonvolatile matter of 15%, the Brookfield viscosity of 630cps in 25 degrees C, 10% [ of nonvolatile matters ], and a Brookfield viscosity [ in 25 degrees C ] of 170cps was obtained after dropping termination by continuing a polymerization for 3 hours, adding water, cooling further, and terminating a reaction at 80 degrees C. This polymer is set to A-3. Many physical-properties values of A-3 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 4 aforementioned reaction container for 177.0g of pure water.

[0068] On the other hand, the mixed dissolution of the 0.544g of the 4 and 4'-azobis-4-cyano valeric acids of 750.7g [ of 50% acrylamide water solutions ] and methylenebis acrylamide 0.837g, 23.8g of sodium methallylsulfonate, and 84% of pure parts was carried out, and monomer initiator mixed liquor was adjusted.

[0069] Then, equal dropping was carried out, having monomer initiator applied [ this ] it for 150 minutes into the reaction container. In the meantime, the temperature in a reaction container was kept at 80 degrees C. Moreover, the temperature of monomer initiator mixed liquor is kept at 20 degrees C or less, and it was made for a polymerization not to produce it before dropping.

[0070] The acrylamide system polymer water solution with the nonvolatile matter of 15%, the Brookfield viscosity of 550cps in 25 degrees C, 10% [ of nonvolatile matters ], and a Brookfield viscosity [ in 25 degrees C ] of 150cps was obtained after dropping termination by continuing a polymerization for 3 hours, adding water, cooling further, and terminating a reaction at 80 degrees C. This polymer is set to A-4. Many physical-properties values of A-4 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 5 aforementioned reaction container for 395.8g of pure water.

[0071] On the other hand, the mixed dissolution of the 0.9g of the 4 and 4'-azobis-4-cyano valeric acids of 339.4g [ of 40% acrylamide water solutions ] and methylenebis acrylamide 4.62g, 9.48g of sodium methallylsulfonate, and 84% of pure parts was carried out, and monomer initiator mixed liquor was adjusted.

[0072] Then, equal dropping was carried out, having monomer initiator applied [ this ] it for 150 minutes into the reaction container. In the meantime, the temperature in a reaction container was kept at 80 degrees C. Moreover, the temperature of monomer initiator mixed liquor is kept at 20 degrees C or less, and it was made for a polymerization not to produce it before dropping.

[0073] The acrylamide system polymer water solution with the nonvolatile matter of 15%, the Brookfield viscosity of 106cps in 25 degrees C, 10% [ of nonvolatile matters ], and a Brookfield viscosity [ in 25 degrees C ] of 38cps was obtained after dropping termination by continuing a polymerization for 3 hours, adding water, cooling further, and terminating a reaction at 80 degrees C. This polymer is set to A-5. Many physical-properties values of A-5 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example of comparison 1 aforementioned reaction container for 500g of pure water.

[0074] On the other hand, 0.9g of the 4 and 4'-azobis-4-cyano valeric acid of 84% of pure parts was dissolved in 355.4g of acrylamide water solutions 40%, and the monomer initiator mixed liquor which added 60g of water was adjusted.

[0075] Then, equal dropping was carried out, having monomer initiator applied [ this ] it for 150 minutes into the reaction container. In the meantime, the temperature in a reaction container was kept at 80 degrees C. Moreover, the temperature of monomer initiator mixed liquor is kept at 20 degrees C or less, and it was made for a polymerization not to produce it before dropping.

[0076] The acrylamide system polymer water solution with the nonvolatile matter of 15%, the Brookfield viscosity of 30000cps in 25 degrees C, 10% [ of nonvolatile matters ], and a Brookfield viscosity [ in 25 degrees C ] of 2820cps was obtained after dropping termination by continuing a polymerization for 3 hours, adding water, cooling further, and terminating a reaction at 80 degrees C. This polymer is set to C-1. Many physical-properties values of C-1 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example of comparison 2 aforementioned reaction container for 500g of pure water.

[0077] Although 355.0g of 40% acrylamide water solutions, the solution which carried out the mixed dissolution of the methylenebis acrylamide 0.308g, and 60g of water solutions which dissolved 0.18g of the 4 and 4'-azobis-4-cyano valeric acid of 84% of pure parts were adjusted further on the other hand and equal dropping was carried out like the example 1 into the reaction container, respectively, it was in the middle of dropping, and the fluidity of reaction mixture was lost and it gelled. This gelation polymer is set to C-2. Even if it diluted C-2 more than it, the distributed dissolution of it was not able to be carried out, and it was not able to measure many physical-properties values.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example of comparison 3 aforementioned reaction container for 500g of pure water.

[0078] On the other hand, 0.9g of the 4 and 4'-azobis-4-cyano valeric acid of 355.0g [ of 40% acrylamide water solutions ] and methylenebis acrylamide 0.308g and 84% of pure parts was dissolved, and the monomer initiator mixed liquor which added 60g of water was adjusted.

[0079] Then, equal dropping was carried out, having monomer initiator applied [ this ] it for 150 minutes into the reaction container. In the meantime, the temperature in a reaction container was kept at 80 degrees C. Moreover, the temperature of monomer initiator mixed liquor is kept at 20 degrees C or less, and it was made for a polymerization not to arise before dropping.

[0080] The acrylamide system polymer water solution with the nonvolatile matter of 15%, the Brookfield viscosity of 15000cps in 25 degrees C, 10% [ of nonvolatile matters ], and a Brookfield viscosity [ in 25 degrees C ] of 1400cps was obtained after dropping termination by continuing a polymerization for 3 hours, adding water, cooling further, and terminating a reaction at 80 degrees C. This polymer is set to C-3. Many physical-properties values of C-3 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example of comparison 4 aforementioned reaction container for 395.8g of pure water.

[0081] On the other hand, although the mixed dissolution was carried out and equal dropping of the 0.9g of the 4 and 4'-azobis-4-cyano valeric acid of 348.3g [ of 40% acrylamide water solutions ] and methylenebis acrylamide 4.62g and 84% of pure parts was carried out like the example 4 into the reaction container, it was in the middle of dropping, and the fluidity of reaction mixture was lost and it gelled. This gelation polymer is set to C-4. Even if it diluted C-4 more than it, the distributed dissolution of it was not able to be carried out, and it was not able to measure many physical-properties values.

[0082] The polymer A-1 to A-5, the presentation of C-1 to C-4, and many physical-properties values which were acquired in examples 1-5 and the examples 1-4 of a comparison were collectively shown in Table 1 and 2 [Tables 1 and 2].

[0083]

[Table 1]

	組成 (モル%)			1) 重合開始剤 (g/モル)	ポリマーNo
	AM	SMS	MBA		
実施例 1	99.7	0.2	0.1	0.09	A-1
実施例 2	99.35	0.25	0.4	0.45	A-2
実施例 3	98.6	1.3	0.1	0.10	A-3
実施例 4	97.13	2.77	0.1	0.10	A-4
実施例 5	95.5	3.0	1.5	0.45	A-5
比較例 1	100			0.45	C-1
比較例 2	99.9		0.1	0.09	C-2
比較例 3	99.9		0.1	0.45	C-3
比較例 4	98.5		1.5	0.45	C-4

AM: アクリルアミド、

SMS: メタリルスルホン酸ナトリウム、

MBA: メチレンビスアクリルアミド、

1) 4, 4'-アゾビス-4-シアノ吉草酸

[0084]

[Table 2]

ポリマー	15% 製品 (cps /25℃)	10% 製品 (cps /25℃)	重量平均 分子量 (a) (万)	重量平均 慣性半径 (b) (nm)	(b) — (a)	数平均 分子量 (c) (万)	(a) — (c)	分子量 100 万 以上 (%)	水和径 (nm)
A-1	18000	1780	305	73.8	0.0000242	125	2.44	73.5	120
A-2	2170	330	339	80.2	0.0000237	38.0	3.85	74.0	170
A-3	630	170	312	72.2	0.0000231	113	2.76	71.8	240
A-4	550	150	315	77.0	0.0000244	105	3.00	66.7	170
A-5	106	38	206	61.5	0.0000299	51.3	4.02	41.4	93
C-1	30000	2820	69.4	35.2	0.0000507	32.2	2.16	18.9	37
C-2	ゲル化								
C-3	15000	1400	64.9	30.1	0.0000464	27.8	2.33	18.4	28
C-4	ゲル化								

C-1 および C-3 の水和径は、コールター N 4 の散乱強度 (カウンタ数) が 50000 以下であり、本来測定できないが、散乱強度 50000 以下における参考値を示す。

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 6 aforementioned reaction container for 600g of pure water.

[0085] On the other hand, the mixed dissolution of 332.8g [ of 40% acrylamide water solutions ] and methylenebis acrylamide 0.308g, 0.79g [ of sodium methallylsulfonate ], N, and N-dimethylaminoethyl METARI rate 12.6g and the 5.2g of the itaconic acids was carried out, and pH was adjusted to 4.2 by HCl 35%.

[0086] Moreover, 60g of water solutions which dissolved 0.16g of 4 and 4'-azobis-4-cyano valeric acids of 84% of pure parts was adjusted.

[0087] Next, equal dropping was carried out, having poured [ above-mentioned / both ] it for 150 minutes into the reaction container, respectively. In the meantime, the temperature in a reaction container was kept at 80 degrees C.

[0088] The acrylamide system polymer water solution with the nonvolatile matter of 15%, the Brookfield viscosity of 5000cps in 25 degrees C, 10% [ of nonvolatile matters ], and a Brookfield viscosity [ in 25 degrees C ] of 960cps was obtained after dropping termination by adding water and adjusting a nonvolatile matter at 80 degrees C, while continuing a polymerization for 3 hours,

cooling and terminating a reaction. This polymer is set to A-6. Many physical-properties values of A-6 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 7 aforementioned reaction container for 660g of pure water.

[0089] On the other hand, the mixed dissolution of the 0.9g of the 4 and 4'-azobis-4-cyano valeric acids of 331.8g [ of 40% acrylamide water solutions ] and methylenebis acrylamide 1.23g, 0.79g [ of sodium methallylsulfonate ], N, and N-dimethylaminoethyl METARI rate 12.6g, 5.2g of itaconic acids, and 84% of pure parts was carried out, pH adjustment was carried out by HCl 35%, and the monomer initiator mixed liquor of pH4.2 was obtained.

[0090] Next, equal dropping was carried out, having monomer initiator applied [ above-mentioned ] it for 150 minutes into the reaction container. In the meantime, the temperature in a reaction container was kept at 80 degrees C. Moreover, the temperature of monomer initiator mixed liquor is kept at 20 degrees C or less, and it was made for a polymerization not to arise before dropping.

[0091] The acrylamide system polymer water solution with the nonvolatile matter of 15%, the Brookfield viscosity of 3000cps in 25 degrees C, 10% [ of nonvolatile matters ], and a Brookfield viscosity [ in 25 degrees C ] of 620cps was obtained after dropping termination by adding water and adjusting a nonvolatile matter at 80 degrees C, while continuing a polymerization for 3 hours, cooling and terminating a reaction. This polymer is set to A-7. Many physical-properties values of A-7 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 8 aforementioned reaction container for 580g of pure water.

[0092] On the other hand, the mixed dissolution of 325.7g [ of 40% acrylamide water solutions ] and methylenebis acrylamide 0.308g, 0.79g of sodium methallylsulfonate, 12.5g of N,N-dimethylaminopropyl acrylamide, and the 7.2g of the 80% acrylic acids was carried out, and pH was adjusted to 4.2 by HCl 35%.

[0093] Moreover, 60g of water solutions which dissolved 0.16g of 4 and 4'-azobis-4-cyano valeric acids of 84% of pure parts was adjusted.

[0094] Next, equal dropping was carried out, having poured [ above-mentioned / both ] it for 150 minutes into the reaction container, respectively. In the meantime, the temperature in a reaction container was kept at 80 degrees C.

[0095] The acrylamide system polymer water solution with the nonvolatile matter of 15%, the Brookfield viscosity of 11000cps in 25 degrees C, 10% [ of nonvolatile matters ], and a Brookfield viscosity [ in 25 degrees C ] of 1980cps was obtained after dropping termination by adding water and adjusting a nonvolatile matter at 80 degrees C, while continuing a polymerization for 3 hours, cooling and terminating a reaction. This polymer is set to A-8. Many physical-properties values of A-8 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 9 aforementioned reaction container for 387g of pure water.

[0096] On the other hand, the mixed dissolution of 414.6g [ of 40% acrylamide water solutions ] and methylenebis acrylamide 0.385g, 2.25g [ of sodium methallylsulfonate ], N, and N-dimethylaminoethyl methacrylate 15.7g and the 6.5g of the itaconic acids was carried out, and pH was adjusted to 4.2 by HCl 35%.

[0097] Moreover, 60g of water solutions which dissolved NaOH of 0.25g of 4 and 4'-azobis-4-cyano valeric acids of 84% of pure parts, and it and 2 double mol was adjusted.

[0098] Next, equal dropping was carried out, having poured [ above-mentioned / both ] it for 150 minutes into the reaction container, respectively. In the meantime, the temperature in a reaction container was kept at 80 degrees C.

[0099] The acrylamide system polymer water solution with the nonvolatile matter of 15%, the Brookfield viscosity of 1500cps in 25 degrees C, 10% [ of nonvolatile matters ], and a Brookfield viscosity [ in 25 degrees C ] of 340cps was obtained after dropping termination by adding water and adjusting a nonvolatile matter at 80 degrees C, while continuing a polymerization for 3 hours, cooling and terminating a reaction. This polymer is set to A-9. Many physical-properties values of A-9 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example of comparison 5 aforementioned reaction container for 660g of pure water.

[0100] On the other hand, the mixed dissolution of the 0.9g of the 4 and 4'-azobis-4-cyano valeric acids of 333.7g [ of 40% acrylamide water solutions ] and methylenebis acrylamide 0.308g, N, and N-dimethylaminoethyl METARI rate 12.6g, 5.2g of itaconic acids, and 84% of pure parts was carried out, and pH was adjusted to 4.2 by HCl 35%.

[0101] Next, equal dropping was carried out, having poured [ above-mentioned ] it for 150 minutes into the reaction container. In the meantime, the temperature in a reaction container was kept at 80 degrees C.

[0102] The acrylamide system polymer water solution with the nonvolatile matter of 15%, the Brookfield viscosity of 9200cps in 25 degrees C, 10% [ of nonvolatile matters ], and a Brookfield viscosity [ in 25 degrees C ] of 630cps was obtained after dropping termination by adding water and adjusting a nonvolatile matter at 80 degrees C, while continuing a polymerization for 3 hours, cooling and terminating a reaction. This polymer is set to C-5. Many physical-properties values of C-5 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example of comparison 6 aforementioned reaction container for 600g of pure water.

[0103] On the other hand, the mixed dissolution of 333.7g [ of 40% acrylamide water solutions ] and methylenebis acrylamide 0.308g, N, and N-dimethylaminoethyl METARI rate 12.6g and the 5.2g of the itaconic acids was carried out, and pH was adjusted to 4.2 by HCl 35%.

[0104] Moreover, 60g of water solutions which dissolved 0.16g of 4 and 4'-azobis-4-cyano valeric acids of 84% of pure parts was adjusted.

[0105] Next, although equal dropping of both the above-mentioned water solutions was carried out like the example 6 into the reaction container, respectively, it was in the middle of dropping, and the fluidity of reaction mixture was lost and it gelled. This gelation polymer is set to C-6. Even if it diluted C-6 more than it, the distributed dissolution of it was not able to be carried out, and it was not able to measure many physical-properties values.

The mixed dissolution of 333.7g [ of 40% acrylamide water solutions ] and methylenebis acrylamide 0.308g, N, and N-dimethylaminoethyl METARI rate 12.6g, 5.2g of itaconic acids, and the 660g of the water was carried out, and pH was adjusted to the example of comparison 7 aforementioned reaction container by HCl 35% 4.2.

[0106] Next, it is the above-mentioned mixed liquor in a reaction container N2 The reaction container was kept warm, after deoxidizing by gas and carrying out the temperature up of the solution temperature to 45 degrees C.

[0107] Subsequently, stirring, 1.32g of ammonium persulfates and 0.6g of sodium hydrogensulfites were added, and the polymerization was made to start. Solution temperature amounted to 80 degrees C after 60 minutes, and it was left at 80 degrees C after that for 1 hour. Then, while cooling and terminating the reaction, the acrylamide system polymer water solution with the nonvolatile matter of 15%, the Brookfield viscosity of 8700cps in 25 degrees C, 10% [ of nonvolatile matters ], and a Brookfield viscosity [ in 25 degrees C ] of 1700cps was obtained by adding water and adjusting a nonvolatile matter. This polymer is set to C-7. Many physical-properties values of C-7 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example of comparison 8 aforementioned reaction container for 660g of pure water.

[0108] On the other hand, the mixed dissolution of the 0.9g of the 4 and 4'-azobis-4-cyano valeric acids of 332.7g [ of 40% acrylamide water solutions ] and methylenebis acrylamide 1.23g, N, and N-dimethylaminoethyl METARI rate 12.6g, 5.2g of itaconic acids, and 84% of pure parts was carried out, and pH was adjusted to 4.2 by HCl 35%.

[0109] Next, although equal dropping of the above-mentioned water solution was carried out like the example 7 into the reaction container, it was in the middle of dropping, and the fluidity of reaction mixture was lost and it gelled. This gelation polymer is set to C-8. Even if it diluted C-8 more than it, the distributed dissolution of it was not able to be carried out, and it was not able to measure many physical-properties values.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the

example of comparison 9 aforementioned reaction container for 660g of pure water.

[0110] On the other hand, the mixed dissolution of the 0.9g of the 4 and 4'-azobis-4-cyano valeric acids of allyl alcohol 9.85g and 84% of pure parts was carried out as 332.7g [ of 40% acrylamide water solutions ], and methylenebis acrylamide 1.23g, N, and N-dimethylaminoethyl METARI rate 12.6g, 5.2g of itaconic acids, and a molecular-weight regulator, and pH was adjusted to 4.2 by HCl 35%.

[0111] Next, equal dropping was carried out, having poured [ above-mentioned ] it for 150 minutes into the reaction container. In the meantime, the temperature in a reaction container was kept at 80 degrees C.

[0112] The nonvolatile matter of 15%, the Brookfield viscosity of 10000cps in 25 degrees C, 10% of nonvolatile matters, and the acrylamide system polymer water solution of Brookfield viscosity [ of 1860cps ] \*\* in 25 degrees C were obtained after dropping termination by adding water and adjusting a nonvolatile matter at 80 degrees C, while continuing a polymerization for 3 hours, cooling and terminating a reaction. This polymer is set to C-9. Many physical-properties values of C-9 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example of comparison 10 aforementioned reaction container for 560g of pure water.

[0113] On the other hand, the mixed dissolution of the 325.7g [ of 40% acrylamide water solutions ] and methylenebis acrylamide 0.308g, 2.6g [ of 25% sodium vinylsulfonate water solutions ], 12.5g [ of N,N-dimethylaminopropyl acrylamide ], 7.2g [ of 80% acrylic acids ], and isopropyl alcohol 23g was carried out, and pH was adjusted to 4.2 by HCl 35%.

[0114] Moreover, 60g of water solutions which dissolved 0.16g of 4 and 4'-azobis-4-cyano valeric acids of 84% of pure parts was adjusted.

[0115] Next, equal dropping was carried out, having poured [ above-mentioned / both ] it for 150 minutes into the reaction container, respectively. In the meantime, the temperature in a reaction container was kept at 80 degrees C.

[0116] The nonvolatile matter of 15%, the Brookfield viscosity of 6800cps in 25 degrees C, 10% of nonvolatile matters, and the acrylamide system polymer water solution of Brookfield viscosity [ of 170cps ] \*\* in 25 degrees C were obtained after dropping termination by adding water and adjusting a nonvolatile matter at 80 degrees C, while continuing a polymerization for 3 hours, cooling and terminating a reaction. This polymer is set to C-10. Many physical-properties values of C-10 were measured like the example 1.

[0117] The polymer A-6 to A-9, the presentation of C-5 to C-10, and many physical-properties values which were acquired in examples 6-9 and the examples 5-10 of a comparison were collectively shown in Tables 3 and 4 [Tables 3 and 4].

[0118]

[Table 3]



	組 成 (モル%)						1) 重合開始剤 (g/モル)	ポリマー No
実施例 6	AM 93.7	DM 4	IA 2	SMS 0.25	MBA 0.1		0.08	A-6
実施例 7	AM 93.35	DM 4	IA 2	SMS 0.25	MBA 0.4		0.45	A-7
実施例 8	AM 91.65	DMA PA 4	AA 4	SMS 0.25	MBA 0.1		0.08	A-8
実施例 9	AM 93.33	DM 4	IA 2	SMS 0.57	MBA 0.1		0.10	A-9
比較例 5	AM 93.9	DM 4	IA 2		MBA 0.1		0.45	C-5
比較例 6	AM 93.9	DM 4	IA 2		MBA 0.1		0.08	C-6
比較例 7	AM 93.9	DM 4	IA 2		MBA 0.1	レファス 系		C-7
比較例 8	AM 93.6	DM 4	IA 2		MBA 0.4		0.45	C-8
比較例 9	AM 93.6	DM 4	IA 2		MBA 0.4		0.45 2)	C-9
比較例 10	AM 91.65	DMA PA 4	AA 4	VS 0.25	MBA 0.1		0.08 3)	C-10

AM: アクリルアミド、 DM: N, N-ジメチルアミノエチルメタアクリレート、 IA: イタコン酸、  
 SMS: メタリルスルホン酸ナトリウム、 MBA: メチレンビスアクリルアミド、  
 DMA PA: N, N-ジメチルアミノプロピルアクリルアミド、 AA: アクリル酸、  
 VS: ビニルスルホン酸ナトリウム

1) 4, 4'-アゾビス-4-シアノ吉草酸  
 2) アリルアルコール使用 3) イソプロピルアルコール使用

[0119]

[Table 4]

	15% 製品 (cps /25℃)	10% 製品 (cps /25℃)	重量平均 分子量 (a) (万)	重量平均 慣性半径 (b) (nm)	(b) —— (a)	数平均 分子量 (c) (万)	(a) —— (c)	分子量 100 万 以上 (%)	水和径 (nm)
A-6	5000	960	359	94.6	0.0000264	131	2.74	74.5	140
A-7	3000	620	407	93.1	0.0000228	104	3.91	65.2	200
A-8	11000	1980	340	90.6	0.0000266	123	2.76	73.0	150
A-9	1500	340	292	75.0	0.0000257	101	2.89	65.7	140
C-5	9200	1630	84.5	38.8	0.0000459	36.9	2.29	27.8	86
C-6	ゲル化								
C-7	8700	1700	91.0	49.9	0.0000548	39.0	2.33	26.9	156
C-8	ゲル化								
C-9	10000	1860	121	57.1	0.0000472	41.0	2.95	33.1	65
C-10	6800	1170	90	43.0	0.0000478	35.0	2.57	26.4	78

C-5~C-10の水和径は、コールターN4の散乱強度(カウンタ数)が5000以下であり、本来測定できないが、散乱強度5000以下における参考値を示す。

Next, the application at the time of using the polymer obtained in the example and the example of a comparison as an internal form force enhancement agent is shown.  
 1% slurry of L-BKP of the degree of beating (Canadian standard freeness) CSF 400 obtained from the application 1 corrugated-paper waste paper -- a sulfuric-acid band -- 0.5% for pulp -- it added and stirred for 3 minutes. pH of the pulp slurry at this time was 6.0. then -- while stirring -- 1% water solution of a polymer A-6 -- nonvolatile matter criteria -- 0.5% for pulp -- it added and stirring was further continued for 3 minutes. After an appropriate time, measurement of freeness (JIS-P8112) and paper making with a TAPPI square shape sheet machine were performed using the obtained pulp slurry. 110 degrees C dries for 3 minutes with a drum dryer, and the wet sheet which carried out paper making is basis-weight 100 g/m<sup>2</sup>. The handmade paper was obtained. the ratio after carrying out gas conditioning of the obtained \*\*\*\* in 20 degrees C and RH65% of air conditioned room for 24 hours or more -- bursting strength (JIS-P8112) and Z-axis reinforcement (JAPAN TAPPI00000) were measured. A polymer A-7 to A-9 and a polymer C-5, C-7, C-9, and actuation with the same said of C-10 were performed. The result was shown in Table 5 [Table 5].

[0120]

[Table 5]

	ポリマー	ろ水度 (ml)	比破裂強度	Z軸強度 (kg・cm)
	無添加	420	3.30	3.15
実 施 例	A-6	460	4.44	5.90
	A-7	480	4.50	6.00
	A-8	455	4.40	5.91
	A-9	450	4.35	5.88
比 較 例	C-5	430	3.90	4.20
	C-7	445	3.88	4.50
	C-9	440	3.87	4.44
	C-10	440	3.94	4.30

[0121]

[Effect of the invention -1] The acrylamide system polymer by this invention of having physical properties as shown in Tables 2 and 4, and structure is clear. Moreover, although a part of conventional technique was mentioned as the example of a comparison, neither of the polymerizations can obtain the polymer which has such new structure and a physical-properties value.

[0122] Furthermore, as a result, as shown in the application (Table 5), there is also no paper durability on-the-strength manifestation effectiveness in the former, and it turns out that the acrylamide system polymer by this invention is high.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 10 aforementioned reaction container for 306g of pure water.

[0123] 60g of water solutions which, on the other hand, dissolved 0.24g of 4 and 4'-azobis-4-cyano valeric acids of the solution which carried out the mixed dissolution of 283g [ of acrylamide water solutions ] and methylenebis acrylamide 0.31g and the 1.58g of the sodium methallylsulfonate 50%, and 84% of pure parts was adjusted, it applied for 150 minutes into the reaction container, respectively, and equal dropping was carried out. In the meantime, the temperature in a reaction container was kept at 80 degrees C. The acrylamide system polymer water solution with a Brookfield viscosity [ in 25 degrees C ] of 12000cps was obtained after dropping termination by continuing a polymerization for 3 hours, cooling at 80 degrees C, and terminating a reaction. This polymer is set to A-10. It was 23.8% when asked for bone-dry polymer concentration by weighing 1g precisely in the aluminum cup of weight known of A-10, and drying it with 105-degree C hot air drying equipment after dilution with about 1g pure water for 3 hours. Moreover, it was 1,760,000 when the weight average molecular weight of A-10 was measured by the above-mentioned approach.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 11 aforementioned reaction container for 288g of pure water.

[0124] On the other hand, the mixed dissolution of the 0.24g of the 4 and 4'-azobis-4-cyano valeric acids of 283g [ of 50% acrylamide water solutions ] and methylenebis acrylamide 0.31g, 1.58g of sodium methallylsulfonate, and 84% of pure parts was carried out, and a monomer and initiator mixed liquor were adjusted.

[0125] Then, equal dropping was carried out, having initiator applied [ this monomer and ] them for 150 minutes into the reaction container. In the meantime, the temperature in a reaction container was kept at 80 degrees C. Moreover, it was careful of the temperature of a monomer and initiator mixed liquor for a monomer not to deposit so that it might keep at 15-25 degrees C and a polymerization might not arise before dropping. The monomer before dropping and the existence of polymerization generating of initiator mixed liquor left the mixed liquor of these conditions for 2 hours, and it was checked from adding in a methanol.

[0126] The acrylamide system polymer water solution with a Brookfield viscosity [ in 25 degrees C ] of 3340cps was obtained after dropping termination by continuing a polymerization for 3 hours, cooling at 80 degrees C, and terminating a reaction. This polymer is set to A-11. Many physical-properties values of A-11 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 12 aforementioned reaction container for 293g of purity.

[0127] On the other hand, they are 2823g [ of 50% acrylamide water solutions ], and methylenebis acrylamide 0.31g, sodium methallylsulfonate 3.18g and 2, and 2'-azobis-2-methyl-N, -(2-hydroxyethyl)- The water solution which carried out the mixed dissolution of the propione amide 0.25g was adjusted, it applied for 150 minutes into the reaction container, and equal dropping was carried out. In the meantime, the temperature of a monomer and an initiator mixed solution kept the temperature in a reaction container at 80 degrees C during dropping again at 15-25 degrees C.

[0128] The acrylamide system polymer water solution with a Brookfield viscosity [ in 25 degrees C ] of 3770cps was obtained after dropping termination by continuing a polymerization for 3 hours, cooling at 80 degrees C, and terminating a reaction. This polymer is set to A-12. Many physical-properties values of A-12 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 13 aforementioned reaction container for 296g of pure water.

[0129] On the other hand, the water solution which carried out the mixed dissolution of the 0.36g of the 4 and 4'-azobis-4-cyano valeric acids of 421g [ of 50% acrylamide water solutions ] and methylenebis acrylamide 0.46g, 6.22g of sodium methallylsulfonate, and 84% of pure parts was adjusted, it applied for 150 minutes into the reaction container, and equal dropping was carried out. In the meantime, the temperature of a monomer and initiator mixed liquor kept constant 80 degrees C of temperature in a reaction container at 15-25 degrees C during dropping.

[0130] The acrylamide system polymer water solution with a Brookfield viscosity [ in 25 degrees C ] of 20000cps was obtained after dropping termination by continuing a polymerization for 3 hours, cooling at 80 degrees C, and terminating a reaction. This polymer is set to A-13. Many physical-properties values of A-13 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 14 aforementioned reaction container for 325g of pure water.

[0131] On the other hand, the mixed dissolution of the 0.93g of the 4 and 4'-azobis-4-cyano valeric acids of 550g [ of 50% acrylamide water solutions ] and methylenebis acrylamide 14.4g, 111g of sodium methallylsulfonate, and 84% of pure parts was carried out, and a monomer and initiator mixed liquor were adjusted.

[0132] Then, equal dropping was carried out, having monomer initiator applied [ this ] it for 150 minutes into the reaction container. In the meantime, the temperature in a reaction container was kept at 80 degrees C. Moreover, the temperature of monomer initiator mixed liquor was kept at 15-25 degrees C.

[0133] The acrylamide system polymer water solution with a Brookfield viscosity [ in 25 degrees C ] of 1070cps was obtained after dropping termination by continuing a polymerization for 3 hours, cooling at 80 degrees C, and terminating a reaction. This polymer is set to A-14. Many physical-properties values of A-14 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 15 aforementioned reaction container for 203g of pure water.

[0134] On the other hand, the mixed dissolution of the 0.66g of the 4 and 4'-azobis-4-cyano valeric acids of 747g [ of 60% acrylamide water solutions ] and methylenebis acrylamide 1.02g, 52.8g of sodium methallylsulfonate, and 84% of pure parts was carried out, and the monomer and the initiator mixed solution were adjusted.

[0135] Then, equal dropping was carried out, having initiator covered [ this monomer and ] them for 150 minutes into the reaction container. In the meantime, the temperature of a monomer and an initiator mixed solution kept the temperature in a reaction container at 80 degrees C again at 15-25 degrees C.

[0136] The acrylamide system polymer water solution with a Brookfield viscosity [ in 25 degrees

C ] of 47600cps was obtained after dropping termination by continuing a polymerization for 3 hours, cooling at 80 degrees C, and terminating a reaction. This polymer is set to A-15. Many physical-properties values of A-15 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example of comparison 11 aforementioned reaction container for 363g of pure water.

[0137] On the other hand, equal dropping was carried out, having poured [ which carried out the mixed dissolution of the 0.24g of the 4 and 4'-azobis-4-cyano valeric acid of 284g / of 50% acrylamide water solutions /, and methylenebis acrylamide 0.31g, and 84% of pure parts ] it for 150 minutes into the reaction container. In the meantime, the mixed solution kept constant 80 degrees C of temperature in a reaction container at 15-25 degrees C or less during dropping. However, in the middle of dropping, reaction mixture became hyperviscosity, and the fluidity of it was lost, and, finally it was gelled. This gelation object is set to C-11. Even if it diluted C-11 with water more than it, the distributed dissolution of it was not able to be carried out, and it was not able to acquire many physical-properties values.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example of comparison 12 aforementioned reaction container for 228g of pure water.

[0138] Equal dropping was carried out having poured [ which, on the other hand, dissolved 0.24g of the 4 and 4'-azobis-4-cyano valeric acid of the solution which mixed 283g / of acrylamide water solutions /, and methylenebis acrylamide 0.31g and isopropyl alcohol 30g 50%, and 84% of pure parts / 60g ] it for 150 minutes into the reaction container, respectively. In the meantime, the temperature in a reaction container was kept at 80 degrees C.

[0139] The acrylamide system polymer water solution with a Brookfield viscosity [ in 25 degrees C ] of 13300cps was obtained after dropping termination by continuing a polymerization for 3 hours, cooling at 80 degrees C, and terminating a reaction. This polymer is set to C-12. Many physical-properties values of C-12 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example of comparison 13 aforementioned reaction container for 217g of pure water.

[0140] On the other hand, equal dropping was carried out, having poured [ which carried out the mixed dissolution of the 1.96g of the 4 and 4'-azobis-4-cyano valeric acids of 766g / of 50% acrylamide water solutions /, and methylenebis acrylamide 17.0g, and 84% of pure parts ] it for 150 minutes into the reaction container. In the meantime, the temperature of a monomer and an initiator mixed solution kept the temperature in a reaction container at 80 degrees C at 15-25 degrees C. However, it was in the middle of dropping, and reaction mixture became hyperviscosity, and the fluidity of it was lost, and it was gelled. This gelation object is set to C-13. Even if it diluted C-13 with water more than it, the distributed dissolution of it was not able to be carried out, and it was not able to acquire many physical-properties values.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example of comparison 14 aforementioned reaction container for 167g of pure water.

[0141] On the other hand, equal dropping was carried out, having covered [ which carried out the mixed dissolution of the 0.84g of the 4 and 4'-azobis-4-cyano valeric acids of 8312g / of 60% acrylamide water solutions /, and methylenebis acrylamide 1.1g, and 84% of pure parts ] it for 150 minutes. In the meantime, the temperature of a monomer and an initiator mixed solution kept the temperature in a reaction container at 80 degrees C again at 15-25 degrees C. However, it was in the middle of dropping, and reaction mixture became hyperviscosity, and the fluidity of it was lost, and it was gelled. This gelation polymer is set to C-14. Even if it diluted C-14 with water more than it, the distributed dissolution of it was not able to be carried out, and it was not able to acquire many physical-properties values.

[0142] Many physical-properties values of the polymer C-11 obtained in the polymer A-10 to A-15 and the examples 11-14 of a comparison which were acquired in the examples 10-15 - C14 were collectively shown in Table 6 and 7.

[0143]

[Table 6]

	実施例						比較例			
	10	11	12	13	14	15	11	12	13	14
AM (%)	99.4	99.4	98.9	98.6	83	94.9	99.9	99.9	98.0	99.9
MBA (%)	0.1	0.1	0.1	0.1	2.0	0.1	0.1	0.1	2.0	0.1
SMS (%)	0.5	0.5	1.0	1.3	15.0	5.0	0	0	0	0
開始剤 <sup>1)</sup> (g/モル)	A 0.1	A 0.1	B 0.12	A 0.1	A 0.2	A 0.1	A 0.1	A 0.1	A 0.3	A 0.1
DPC <sup>2)</sup> (%)	23.8	27.4	27.4	31.9	43.1	53.9	—	25.6	—	—
粘度 (μs)	120	33.4	37.7	200	10.7	476	ゲル	133	ゲル	ゲル
Mw <sup>3)</sup> (万)	175	90.5	130	312	77.3	62	—	36.6	—	—

1) 開始剤 A : 4, 4'-アゾビス-4-シアノ吉草酸  
B : 2, 2'-アゾビス-2-メチル-N-(2-ヒドロキシエチル)-プロピオンアミド

2) DPC : 絶乾ポリマー濃度

3) Mw : 重量平均分子量

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 16 aforementioned reaction container for 355g of pure water.

[0144] On the other hand, the mixed dissolution of 263g [ of 50% acrylamide water solutions ] and methylenebis acrylamide 0.25g, 1.49g [ of sodium methallylsulfonate ], N, and N-dimethylaminoethyl METARI rate 15.7g and the itaconic acid 5.2 was carried out, and pH was adjusted to 4.2 by HCl 35%.

[0145] Moreover, 60g of water solutions which dissolved 0.24g of 4 and 4'-azobis-4-cyano valeric acids of 84% of pure parts was adjusted.

[0146] Next, equal dropping was carried out, having poured [ above-mentioned / both ] it for 150 minutes into the reaction container, respectively. In the meantime, the temperature in a reaction container was kept at 80 degrees C.

[0147] The acrylamide system polymer water solution with a Brookfield viscosity [ in 25 degrees C ] of 8950cps was obtained after dropping termination by continuing a polymerization for 3 hours, cooling and terminating a reaction at 80 degrees C. This polymer is set to A-16. Many physical-properties values of A-16 were measured like the example 10.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the example 17 aforementioned reaction container for 286g of pure water.

[0148] On the other hand, the mixed dissolution of 394g [ of 50% acrylamide water solutions ] and methylenebis acrylamide 0.46g, 6.30g of sodium methallylsulfonate, 18.8g of N,N-dimethylaminopropyl acrylamide, 5.94g of itaconic acids, and the 5.48g of the acrylic acids was carried out, and pH was adjusted to 4.2 by HCl 35%.

[0149] Moreover, 60g of water solutions which dissolved 0.36g of 4 and 4'-azobis-4-cyano valeric acids of 84% of pure parts was adjusted.

[0150] Next, equal dropping was carried out, having poured [ above-mentioned / both ] it for 150 minutes into the reaction container, respectively. In the meantime, the temperature in a reaction container was kept at 80 degrees C.

[0151] The acrylamide system polymer water solution with a Brookfield viscosity [ in 25 degrees C ] of 12000cps was obtained after dropping termination by continuing a polymerization for 3 hours, cooling and terminating a reaction at 80 degrees C. This polymer is set to A-17. Many physical-properties values of A-17 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into the

example 18 aforementioned reaction container for 173g of pure water.

[0152] On the other hand, the mixed dissolution of 730g [ of acrylamide water solutions ] and methylenebis acrylamide 1.67g, 25.7g of sodium methallylsulfonate, and the 9.75g of the acrylic acids was carried out 50%, and the sulfuric acid adjusted pH to 4.2 40%.

[0153] Moreover, 60g of water solutions which dissolved 1.08g of 2 and 2'-azobis-2-methyl propione amidine hydrochlorides was adjusted.

[0154] Next, equal dropping was carried out, having poured [ above-mentioned / both ] it for 150 minutes into the reaction container, respectively. In the meantime, the temperature in a reaction container was kept at 80 degrees C.

[0155] The acrylamide system polymer water solution with a Brookfield viscosity [ in 25 degrees C ] of 25500cps was obtained after dropping termination by continuing a polymerization for 3 hours, cooling and terminating a reaction at 80 degrees C. This polymer is set to A-18. Many physical-properties values of A-18 were measured like the example 1.

Using 3 opening flask equipped with the agitator, the reflux cooling pipe, and the thermometer as an example of comparison 15 reaction container, the mixed dissolution of 409g [ of pure water ], 263g [ of 50% acrylamide water solutions ], and methylenebis acrylamide 0.19g, N, and N-dimethylaminoethyl METARI rate 15.7g and the 5.21g of the itaconic acids was carried out, and the temperature up of the pH was carried out to 35 degrees C after adjusting to 4.2 by HCl 35%. There, when 1.0g of 2 and 2'-azobis-2-(2-imidazoline-2-IRU) propane hydrochlorides was added there, initiation of a polymerization was checked after the 20 minutes, and whenever [ reaction container internal temperature ] amounted to 93 degrees C after the 20 minutes further. After continuing a polymerization then for 2 hours, the acrylamide system polymer water solution with a Brookfield viscosity [ in 25 degrees C ] of 46100cps was obtained by cooling and terminating a reaction. This polymer is set to C-15. Many physical-properties values of C-15 were measured like the example 1.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into an example of comparison 16 reaction container (said 5 opening flask) for 278g of pure water.

[0156] On the other hand, the mixed dissolution of 397g [ of 50% acrylamide water solutions ] and methylenebis acrylamide 0.31g, N, and N-dimethylaminoethyl METARI rate 23.5g and the 7.8g of the itaconic acids was carried out, and pH was adjusted to 4.2 by HCl 35%.

[0157] Moreover, 60g of water solutions which dissolved 1.07g of 4 and 4'-azobis-4-cyano valeric acids of 84% of pure parts was adjusted.

[0158] Next, although equal dropping of both the above-mentioned water solutions was carried out like the example 10 into the reaction container, respectively, it was in the middle of dropping, and the fluidity of reaction mixture was lost and it gelled. This gelation polymer is set to C-16. Even if it diluted C-16 more than it, the distributed dissolution of it was not able to be carried out, and it was not able to measure many physical-properties values.

The internal temperature was adjusted to 80 degrees C, blowing brewing \*\* nitrogen gas into an example of comparison 17 reaction container (said 5 opening flask) for 330g of pure water.

[0159] On the other hand, the mixed dissolution of the allyl alcohol 23.7g was carried out as 397g [ of 50% acrylamide water solutions ], N, and N-dimethylaminoethyl METARI rate 21.4g, 8.85g of itaconic acids, and a regulator, and pH was adjusted to 4.2 by HCl 35%.

[0160] Moreover, 60g of water solutions which dissolved 0.9g of 4 and 4'-azobis-4-cyano valeric acids of 84% of pure parts was adjusted.

[0161] Next, equal dropping was carried out, having poured [ above-mentioned / both ] it for 150 minutes into the reaction container, respectively. In the meantime, the temperature in a reaction container was kept at 80 degrees C. The acrylamide system polymer water solution with a Brookfield viscosity [ in 25 degrees C ] of 3890cps was obtained after dropping termination by continuing a polymerization for 3 hours, cooling at 80 degrees C, and terminating a reaction. This polymer is set to C-17. Many physical-properties values of C-17 were measured like the example 1.

[0162] Many physical-properties values of the polymer C-15 obtained in the polymer A-16 to A-18 and the examples 15-17 of a comparison which were acquired in the examples 16-18 - C17 were collectively shown in Table 7.

[0163]

[Table 7]

	実 施 例			比 較 例		
	1 6	1 7	1 8	1 5	1 6	1 7
AM (モル%)	92.5	91.1	94.8	92.4	92.9	94.0
MBA (モル%)	0.08	0.1	0.2	0.06	0.1	0
SMS (モル%)	0.47	1.33	3.0	0	0	0
DM <sup>1)</sup> (モル%)	5	4	—	5	5	4
ITA <sup>2)</sup> (モル%)	2	1.5	—	2	2	2
AA <sup>3)</sup> (モル%)	0	2	2	0	0	0
開始剤 <sup>4)</sup> (g/モル)	A 0.1	A 0.1	C 0.2	D 0.5	A 0.3	A 0.22
DPC (%)	22.1	33.2	43.9	23.9	—	31.1
粘度 (ps)	89.5	120	255	461	GEL	38.9
Mw (万)	320	264	184	41.0	—	16.0

1) DM: ジメチルアミノエチルメタクリレート

2) ITA: イタコン酸

3) AA: アクリル酸

4) 開始剤 C: 2, 2'-アゾビス-2-メチルプロピオンアミジン塩酸塩  
D: 2, 2'-アゾビス-2-(2-イミダゾリン-2-イル)

Next, the application at the time of using the polymer obtained in the example and the example of a comparison as an internal form force enhancement agent is shown.

the L-BKP1% slurry of an application 2 - 3CSF400 -- a sulfuric-acid band -- 0.5% for pulp -- it added and stirred for 3 minutes. pH of the pulp slurry at this time was 6.0. then -- while stirring -- 1% water solution of a polymer A-16 -- nonvolatile matter criteria -- 0.5% for pulp -- it added and stirring was further continued for 3 minutes. After an appropriate time, measurement of freshness (JIS-P8112) and paper making with a TAPPI square shape sheet machine were performed using the obtained pulp slurry. 110 degrees C dries for 3 minutes with a drum dryer, and the wet sheet which carried out paper making is basis-weight 100 g/m<sup>2</sup>. The handmade paper was obtained. the ratio after carrying out gas conditioning of the obtained \*\*\*\* in 20 degrees C and RH65% of air conditioned room for 24 hours or more -- bursting strength (JIS-P8112) and Z-axis reinforcement (internal bond-tester and Kumagaya Riki Kogyo K.K. make) were measured. A polymer A-17 and a polymer C-15, and actuation with the same said of C-17 were performed. The result was shown in Table 8.

[0164]

[Table 8]

	添加樹脂	比破裂強度 (Kg/cm <sup>2</sup> )	濾水度 (ml)	Z軸強度 (Kg-cm)
	無添加	3.31	415	3.12
応用例 2	A-7	4.21	465	5.83
応用例 3	A-8	4.33	460	5.76
比較応用例 1	C-5	3.89	430	4.14
比較応用例 2	C-7	3.99	440	4.23

[0165]

[Effect of the invention -2] Though it is the high concentration which is not seen by the former and the amount of macromolecules as shown after the example 10, the acrylamide system polymer water solution by this invention is the aqueous polymerization object of hypoviscosity, although it is high concentration therefore, becomes reducible [ the freight per solid content ], and is economically excellent. Furthermore, when this polymer is used as a paper reinforcing agent, the thing which bring about the conventional paper reinforcing agent and the engine performance more than equivalent and to excel is clear.

Acrylamide 330g, 1g [ of sodium methallylsulfonate ], and methylenebis acrylamide 0.5g and 558g of city waters are added to the 1l. 4-inlet separable flask equipped with example 19 stirrer, a thermometer, a reflux condenser, and nitrogen installation tubing 40%, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 7400cps in 25 degrees C and pH4.2 was obtained. The absolute molecular weight determined by said measuring method was 2,400,000. This product is set to A.

Acrylamide 330g, dimethylaminoethyl methacrylate 14g, 1g [ of sodium methallylsulfonate ], and methylenebis acrylamide 0.5g and 615g of city waters are added to the example 20 aforementioned separable flask 40%, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 7000cps in 25 degrees C and pH4.2 was obtained. The absolute molecular weight determined by said measuring method was 2,500,000. This product is set to B.

40% acrylamide 330g, dimethylaminoethyl methacrylate 16g, 8g [ of 80% acrylic acids ], 3g [ of itaconic acids ], 1g [ of sodium methallylsulfonate ], and methylenebis acrylamide 0.5g and 669g of city waters are added to the example 21 aforementioned separable flask, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 5900cps in 25 degrees C and pH4.2 was obtained. The absolute molecular weight determined by said measuring method was 2,800,000. This product is set to C.

40% acrylamide 330g, dimethylaminoethyl methacrylate 5g, 80%N-METAKURIROIKISHI ethyl trimethylammonium chloride 18g, 10g [ of 80% acrylic acids ], 1g [ of sodium methallylsulfonate ], and methylenebis acrylamide 0.5g and 698g of city waters are added to the example 22 aforementioned separable flask, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 6200cps in 25 degrees C and pH4.2 was obtained. The absolute molecular



weight determined by said measuring method was 2,700,000. This product is set to D. 40% acrylamide 330g, 80%N-methacryloyloxy-ethyl trimethylammonium chloride 25g, 10g [ of 80% acrylic acids ], 1g [ of sodium methallylsulfonate ], and methylenebis acrylamide 0.5g and 710g of city waters are added to the example 23 aforementioned separable flask, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 6800cps in 25 degrees C and pH4.2 was obtained. The absolute molecular weight determined by said measuring method was 2,600,000. This product is set to E.

Acrylamide 330g, 20g [ of 80% acrylic acids ], 1g [ of sodium methallylsulfonate ], and methylenebis acrylamide 0.5g and 645g of city waters are added to the example 24 aforementioned separable flask 40%, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 5400cps in 25 degrees C and pH4.2 was obtained. The absolute molecular weight determined by said measuring method was 2,500,000. This product is set to F. 40% acrylamide 330g, 12g [ of 80% acrylic acids ], 5g [ of itaconic acids ], 1g [ of sodium methallylsulfonate ], and methylenebis acrylamide 0.5g and 615g of city waters are added to the example 25 aforementioned separable flask, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 6100cps in 25 degrees C and pH4.2 was obtained. The absolute molecular weight determined by said measuring method was 2,400,000. This product is set to G. Acrylamide 330g, 1g of sodium methallylsulfonate, and 555g of city waters are added to the example of comparison 18 aforementioned separable flask 40%, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 8300cps in 25 degrees C and pH4.2 was obtained. The absolute molecular weight determined by said measuring method was 700,000. This product is set to H.

Acrylamide 330g, methylenebis acrylamide 0.5g, and 553g of city waters are added to the example of comparison 19 aforementioned separable flask 40%, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 5400cps in 25 degrees C and pH4.2 was obtained. The absolute molecular weight determined by said measuring method was 900,000. This product is set to I.

Acrylamide 330g, dimethylaminoethyl methacrylate 14g, 1g of sodium methallylsulfonate, and 607g of city waters are added to the example of comparison 20 aforementioned separable flask 40%, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 8000cps in 25 degrees C and pH4.2 was obtained. The absolute molecular weight determined by said measuring method was 970,000. This product is set to J.

Acrylamide 330g, dimethylaminoethyl methacrylate 16g, 8g of 80% acrylic acids, 3g of itaconic acids, 1g of sodium methallylsulfonate, and 659g of city waters are added to the example of comparison 21 aforementioned separable flask 40%, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and

carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 6700cps in 25 degrees C and pH4.2 was obtained. The absolute molecular weight determined by said measuring method was 810,000. This product is set to K. 40% acrylamide 330g, dimethylaminoethyl methacrylate 5g, 80%N-methacryloiloxy-ethyl trimethylammonium chloride 18g, 10g of 80% acrylic acids, 1g of sodium methallylsulfonate, and 683g of city waters are added to the example of comparison 22 aforementioned separable flask, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 6000cps in 25 degrees C and pH4.2 was obtained. The absolute molecular weight determined by said measuring method was 1,000,000. This product is set to L.

40% acrylamide 330g, 80%N-methacryloiloxy-ethyl trimethylammonium chloride 25g, 10g of 80% acrylic acids, 1g of sodium methallylsulfonate, and 707g of city waters are added to the example of comparison 23 aforementioned separable flask, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 7100cps in 25 degrees C and pH4.2 was obtained. The absolute molecular weight determined by said measuring method was 1,100,000. This product is set to M. Acrylamide 330g, 20g of 80% acrylic acids, 1g of sodium methallylsulfonate, and 642g of city waters are added to the example of comparison 24 aforementioned separable flask 40%, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 6900cps in 25 degrees C and pH4.2 was obtained. The absolute molecular weight determined by said measuring method was 890,000. This product is set to N.

Acrylamide 330g, 12g of 80% acrylic acids, 5g of itaconic acids, 1g of sodium methallylsulfonate, and 638g of city waters are added to the example 26 aforementioned separable flask 40%, pH is adjusted to 4.2, and the temperature up of the temperature is carried out to 50 degrees C, performing a nitrogen purge. After adding and carrying out the polymerization of the ammonium persulfate for 120 minutes after that, when it cooled and the polymerization reaction was made to complete, the water-soluble stable polymer of the Brookfield viscosity of 73000cps in 25 degrees C and pH4.2 was obtained. The absolute molecular weight determined by said measuring method was 880,000. This product is set to O.

[0166] the pulp slurry of 1.0% of concentration which is degree-of-beating CSF(Canadian standard freeness) 420ml obtained from applications 4-10 and the comparison application 3 - 10 corrugated-paper waste paper -- an aluminum sulfate -- dry weight criteria -- 1.0% for pulp -- it added and stirred for 1 minute. pH of the pulp slurry at this time was 5.0. moreover, actuation that it is the same except adding a sodium hydroxide just before adding an aluminum sulfate -- adjusting -- pH of a pulp slurry -- 5.0 and 6. -- it was 0 and 7.0. Subsequently, 0.5% for pulp was added for the paper reinforcing agent obtained in the example 19 on desiccation criteria, and stirring was continued for 1 more minute. Paper making was carried out with the TAPPI square shape sheet machine using the obtained pulp slurry. The wet sheet which carried out paper making performs 110 degrees C and desiccation during 3 minutes with a drum dryer, and is basis-weight 150 g/m<sup>2</sup>. The handmade paper was obtained. Let this \*\*\*\* be an application 4. JIS after performing seasoning of 24 hours or more for obtained \*\*\*\* in 20 degrees C and RH65% of air conditioned room -- law -- following -- a ratio -- bursting strength (JIS-P8112) and a ratio -- measurement (JIS-P8121) of compressive strength (JIS-P8126) and freshness was performed. The result was shown in Tables 8-10.

[0167] In the approach of obtaining the converted paper of an application 4, the paper of applications 5-10 and the comparison applications 3-10 was completely obtained in the same

conditions and identity operation except changing the paper reinforcing agent (A) of an example 19. moreover, the ratio of the paper of applications 5-10 and the comparison applications 3-10 -- bursting strength and a ratio -- measurement of compressive strength and freshness was also completely performed in the same conditions and identity operation with evaluation of the paper of an application 4.

[0168]

[Table 9]

(抄紙 215.0)

	添加樹脂	比破裂強度 (Kgf/cm <sup>2</sup> )	比圧縮強度 (N・m <sup>2</sup> /g)	濾水度 (ml)
	無添加	3.52	15.3	420
応用例4	A	4.72	19.4	445
応用例5	B	4.81	21.0	465
応用例6	C	4.85	21.4	485
応用例7	D	4.86	21.0	470
応用例8	E	4.80	20.6	480
応用例9	F	4.87	21.6	480
応用例10	G	4.90	21.6	475
比較応用例1	H	4.22	18.1	430
比較応用例2	I	4.24	18.3	440
比較応用例3	J	4.38	18.5	440
比較応用例4	K	4.20	18.2	440
比較応用例5	L	4.21	18.0	430
比較応用例6	M	4.25	18.6	420
比較応用例7	N	4.30	19.0	440
比較応用例8	O	4.31	19.1	435

[0169]

[Table 10]

(抄紙pH6.0)

	添加樹脂	比破裂強度 (Kgf/cm <sup>2</sup> )	比圧縮強度 (N・m <sup>2</sup> /g)	濾水度 (ml)
	無添加	3.65	16.0	425
応用例1	A	4.70	19.5	450
応用例2	B	4.85	21.3	465
応用例3	C	4.91	21.8	460
応用例4	D	4.90	21.5	465
応用例5	E	4.88	21.0	475
応用例6	F	4.80	20.2	470
応用例7	G	4.84	21.0	465
比較応用例1	H	4.25	18.2	420
比較応用例2	I	4.26	18.3	430
比較応用例3	J	4.43	19.0	440
比較応用例4	K	4.25	18.9	430
比較応用例5	L	4.22	18.5	425
比較応用例6	M	4.25	19.0	425
比較応用例7	N	4.26	18.6	450
比較応用例8	O	4.28	19.4	445

[0170]

[Table 11]

(抄紙pH7.0)

	添加樹脂	比破裂強度 (Kgf/cm <sup>2</sup> )	比圧縮強度 (N・m <sup>2</sup> /g)	漉水度 (ml)
	無添加	3.55	15.1	420
応用例 1	A	4.64	19.1	445
応用例 2	B	4.81	21.0	455
応用例 3	C	4.88	21.3	460
応用例 4	D	4.90	21.6	460
応用例 5	E	4.82	20.6	460
応用例 6	F	4.76	20.0	450
応用例 7	G	4.81	20.7	455
比較応用例 1	H	3.92	17.2	425
比較応用例 2	I	3.99	17.9	430
比較応用例 3	J	4.20	18.9	425
比較応用例 4	K	4.22	19.4	430
比較応用例 5	L	4.15	18.0	430
比較応用例 6	M	4.23	18.7	430
比較応用例 7	N	3.89	17.6	440
比較応用例 8	O	3.98	18.4	435

[0171]

[Effect of the invention -3] the paper reinforcing agent of the former [ paper reinforcing agent / by this invention ] -- comparing -- a ratio -- bursting strength and a ratio -- it is clear from the result of Tables 8-10 that it is the outstanding paper reinforcing agent which has the description of the paper durability effectiveness which was excellent in compressive strength and freshness being shown, and being hard to be influenced of pH fluctuation by the paper-milling system.

[Translation done.]